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SULFURIC ACID PLANT EMISSIONS DURING START-UP, SHUTDOWN, AND MALFUNCTION

E. L. Calvin, et al

Catalytic, Incorporated

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16. ABSTRACT The report gives results of a study of dual-absorption contact sulfuric acid plants, as well as single-absorption plants equipped with vent gas cleaning systems for removal of SO2, to determine the relationship between process parameters and air emissions. Processes studied were dual-absorption acid plants and single-absorption acid plants equipped with sodium scrubbers, ammonia scrubbers, and molecular sieve adsorbers. Emissions considered were SO2 and acid mist emissions and vent gas opacity. Relationships were developed for normal operations and compared to off-normal operations such as shutdown, start-up, malfunction, and misoperation. Process parameters and emission relationships are presented in statistical, tabular, and graphic form. Converter bed operating temperature ranges were established and causes of SO2 and acid mist emissions are illustrated from plant operating data.

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Industrial Plants	Sodium	Stationary Sources		
Sulfuric Acid	Ammonia	Molecular Sieves	07B	
Mist	Absorbers			
Sulfur Dioxide	(Materials)			11G
Opacity		PRICES SUBJECT TO CHANGE		

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by

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SECTION I

SUMMARY AND CONCLUSIONS

Data were collected from twelve sulfuric acid plants to establish the relationship between atmospheric emissions (SO_2, acid mist and opacity) and process parameters. The data were collected from single absorption and dual absorption contact acid plants and single absorption plants with tail gas cleaning systems. The tail gas cleaning systems studied were the sodium scrubbing system (Wellman-Lord sodium bisulfite), the ammonia scrubbing system and the molecular sieve absorption system.

Operating parameters were related to emissions during shutdown, start-up, malfunctions and misoperation conditions. Conclusions that can be drawn from the data collected and the plants studied are presented in the table of Summary and Conclusions. Obviously, all malfunctions and all aspects of operations contributing to emissions could not be covered in this study. Those that were covered represent occurrences where data was available at the plants visited.

SUMMARY AND CONCLUSIONS

CAUSE OF TRANSIENT CONDITION	EFFECT ON PROCESS	CORRECTIVE ACTION	FREQUENCY OF OCCURRENCE	DURATION OF CONTROL	STACK EMISSIONS	PREVENTION OR CONTROL	COMMENTS	EXAMPLE
Converter Bed Inlet Temperature Out Of Range Dual Absorption Plant	Conversion Efficiency Reduced	Manual Adjustment of Dampers, Adjustment or Repair of Instruments	Daily	2 Hrs.	SO_2, 400 - 1,000 PPM	Proper Operation and Control and Maintenance	Range of Permissible Variation From Temperature Specifications on Inlet Temperatures is 1 to 3% of Specified Temperature	Table 4A
Planned Shutdown Dual Absorption Plant SAP With Scrubber	Sulfur Feed Stopped and Unit Purged of SO_2 & SO_3	Manual Adjustment of Valves and Controllers	4/Yr. to 1 time/2 Yr.	1 Hour to 2 Weeks	None	Proper Procedure for Shutdown to Facilitate Start-Up	Planned Shutdown Should Not Cause Emissions On Shutdown. Proper Shutdown Minimizes Start-Up Emissions.	Figure 21
Start-Up Dual Absorption Plant	Warm Plant After Short Term Shutdown (< 4 Hrs.)	Preheat of Plant Not Required	12/Yr.	4 Hrs.	< 300 PPM SO_2	Heat Conservation and Proper Start-Up Procedures	SO_2 Concentration Inlet to Converter Most Important to SO_2 Emission Control	Table 11 & 13
Start-Up Dual Absorption Plant	Cold Plant After Long Term Shutdown (> 4 Hrs.)	Plant Must Be Preheated Up to 5 Days	1-2 Times/ Yr.	3-5 Days	< 300 PPM SO_2	Complete Preheat and Reduced SO_2 Inlet Conc. Start-Up Period 4-5 Days Using Proper Start-Up Procedure	SO_2 Concentration Can Be Kept Below NSPS With Sufficient Preheat Time and Low Initial Inlet SO_2 Concentrations. This is Ideal And Seldom Used Because of Production Loss During Long Start-Up. Auxiliary Preheaters Required for Faster Heat Up.	Figure 15
Start-Up Dual Absorption Plant	Cold Plant After Long Term Shutdown (> 4 Hrs.)	Plant Receives Minimum Heat Before SO_2 Addition	1-4 Times/ Yr.	4-6 Hrs.	300 to 3000 PPM SO_2	Minimum Preheat is Applied and Inlet SO_2 Concentration is Started At Full Rate	Start-up Method Most Commonly Used to Minimize Start-Up Time and Product Loss. Balance With Above Method Most Desirable	Table 11 Figure 12 & 16
Misoperation of Sodium and Ammonia Scrubber Systems	Operation at Gas Flow Above Design Limit	Operate Scrubber With Gas Flow Within Design	Daily	1-6 Hrs.	Up to 1,200 PPM SO_2	Reduce Gas Flow Rate. Proper Instruments and Procedures.	Most Common Cause of High SO_2 Emissions is High Gas Flow. More Conservative Design Should Be Employed.	Figure 22 & 23
Misoperation of Ammonia Scrubber Systems	High Gas Flow Rates and Solution Concentration Too Low	Reduce Gas Flow Rate and Increase Solution Concentration	Daily	1-6 Hrs.	Up to 1,200 PPM SO_3	Operate With Gas Flow Within Design and Solution Concentration At 7%. Proper Instruments and Procedures.	Operation With Solution Concentration at 4% (Specified Set Point) Will Reduce NH_3 Consumption But Will Produce High SO_2 Emissions.	Figure 20 & 22

CAUSE OF TRANSIENT CONDITION	EFFECT ON PROCESS	CORRECTIVE ACTION	FREQUENCY OF OCCURRENCE	DURATION OF CONTROL	STACK EMISSIONS	PREVENTION OR CONTROL	COMMENTS	EXAMPLE
Brink Filter On Ammonia Scrubber Outlet Inoperative	High Opacity and High SO_2 Readings On Reich Test	Restore Effective Operation of Brink Filter	1/2 Year	Continuous Until Repaired	SO_2 Reading Up to 3,000 PPM High Opacity	Repair Leak in Brink Filter Internals. Place Booster Blower and Brink in Service.	Brink Sometimes Bypassed on Start-Up Because of Lack of Steam for Booster Blower. Corrosion Can Cause Leak Around Filter Sleeve Connections.	Table 7 & 14
Loss of Sulfur Flow to Furnace	Low SO_2 Inlet Concentration	Restore Burner or Pump Operation or Unplug Burners	Frequent	1-4 Hours Depends Upon Operator	None	Use Clean Sulfur, Proper Sulfur System Maintenance and Operator Attention.	Loss of Sulfur Feed Will Not Cause High SO_2 Unless Extended Period Reduces Converter Temp.	Figure 23
High Sulfur Flow to Furnace	High SO_2 Inlet Concentration	Reduce Sulfur Flow to Furnace or Increase Air for Proper SO_2 Concentration	Frequent	Depends Upon Operator Attention	High SO_2	Control SO_2 Inlet Concentration Consistant with Catalyst Condition	Dual Absorption Plant Normally Uses Higher SO_2 Inlet Concentration Than Single Absorption. Catalyst Condition Limits Concentration.	Figure 23
Loss of Dilution Water to Primary Absorber	Increased Absorber Acid Concentration	Restore Dilution Water Flow to Pump Tank	Infrequent	Continuous Until Repaired	SO_2 Increased Small SO_3 and Opacity Increase	Assure Adequate Supply and Instrument Maintenance. Operator Inspection.	Reduced SO_3 Absorption in Primary Absorber Increases SO_2 Exit Converter by Equilibrium Shift in Succeeding Converter Stages. SO_3 and Opacity May Be Increased.	Figure 23
Loss of Dilution Water to Secondary Absorber	Increased Absorber Acid Concentration	Restore Dilution Water Flow to Pump Tank	Infrequent	Continuous Until Repaired	SO_3 and Opacity Increased	Assure Adequate Supply and Instrument, Maintenance. Operator Inspection.	Secondary Absorber Will Increase SO_3 and Opacity But Will Not Increase SO_2 Emissions	Figure 23
Feed of Dark Sulfur or Sludge Acid	Increased Water in System	Change Feed, Filter Sulfur	----	Continuous Until Feed Change	Acid Mist Increased	Improved Demisters and Filters Such As Brink High Efficiency	Additional Water in System Causes Generation of Acid Mist. Modern Dual Absorption Plants Will Remove Most With Efficient Demisters.	Figure 17 & 19
Feed of Dark Sulfur or Sludge Acid	NO_x Generation in Furnace	Change Feed, Filter Sulfur	----	Continuous Until Feed Change	Acid Mist Increase	Improved Demisters and Filters Such As Brink High Efficiency. Use of ESP	Presence of NO_x in Gas Stream Causes Formation of Acid Mist By Gas Phase Reaction Through Combination With SO_2	----

SECTION II

INTRODUCTION

EPA promulgated emissions standard of performance for a number of stationary sources including sulfuric acid plants on December 23, 1971,(1) based upon steady-state operations. Subsequent revisions(2) to Section 60.7 (c) provide for a quarterly report to be submitted to EPA detailing "--excess emissions as defined in the applicable subparts" (subpart H for sulfuric acid plants of the regulation). "The report shall include the magnitude of excess emissions as measured by the required monitoring equipment reduced to the units of the applicable standard, the date, and time of commencement and completion of each period of excess emissions. Periods of excess emissions due to start-up, shutdown, and malfunction shall be specifically identified. The nature and cause of any malfunction (if known), the corrective action taken, or preventive measures adopted shall be reported".

The standards for new or modified sulfuric acid plants are summarized below:

SULFUR DIOXIDE

No more than 2 kg of sulfur dioxide (SO_2) per metric ton of acid (100 percent H_2SO_4) produced (4.0 pounds per short ton).

ACID MIST

No more than 0.75 kg of acid mist (measured as H_2SO_4) per metric ton of acid (4 lb. per short ton) (100 percent H_2SO_4) produced.

No visible air pollutants shall be released to the atmosphere.

These standards of performance are applied to new contact-process sulfuric acid and oleum facilities that burn elemental sulfur, alkylation acid, hydrogen sulfide, organic sulfides, mercaptans, or acid sludge. They do not apply to metallurgical plants that use acid plants as SO_2 control systems, or to chamber process plants or acid concentrators.

These performance standards were based on tests of sulfuric acid plants, and the judgement of the Environmental Protection Agency is that the standards can be met with present available control systems at a reasonable cost.

PERFORMANCE TESTING

Testing must be performed no later than 60 days after achieving the design production rate, but no longer than 180 days after initial start-up. These tests will be conducted at or above the design production rate.

Owner or operator responsibilities:

1. To perform the tests.
2. Give minimum of ten days notification of scheduled tests.
3. Provide all equipment necessary to conduct tests.

4. Provide safe access to the sampling site.
5. Furnish a written report of the test results.

EPA personnel have the right to perform additional tests at any reasonable time under conditions based on representative performance.

The various testing methods are specified in the standards for each pollutant. Each test consists of three repetitions of the applicable test method. The average of the repetitions will be used to determine compliance.

STACK AND PROCESS MONITORING

The instrumentation required for monitoring stack emissions and production rate is listed below:

1. Oxides of sulfur detector for continuously monitoring the stack. It must read in volume ppm of oxides of sulfur as sulfur dioxide.
2. A suitable flow meter for determining the production rate of sulfuric acid in tons per hour as 100 percent sulfuric acid. An appropriate tank inventory system is also acceptable.

RECORDKEEPING AND REPORTING

All records are to be kept by the facility for two years following the date of measurement and summary. The plant will make available to EPA any records necessary to determine performance. Emission data shall be made available to the public, although no trade secrets, commercial, financial, or other private information will be disclosed.

The items to be recorded, and frequency of data to be recorded is specified in the Standards of Performance.

SECTION III

STUDY OBJECTIVE AND APPROACH

STUDY OBJECTIVE

The objective of this study is to establish the relationship between sulfuric acid plant emissions (SO_2, particulates, and visible emissions) and process parameters for normal production operations and for other operations such as start-up, shutdown, and mechanical malfunctions. The relationships developed are based upon data obtained from actual plant operations representing realistic operating conditions. Theroretical considerations were used only where required to complete the data used to establish the relationships. A maximum use of operating data and statistical analysis using measured emissions has strengthened the reliability of the process operating parameters. The study is intended to establish (to the greatest extent possible) an understanding of the cause and effect relationships between process plant operating parameters and emissions.

The project included the study of contact sulfuric acid plants using double absorption process techniques that are capable of meeting the EPA New Sources Performance Standards (NSPS) under normal operating conditions and those using the tail gas clean-up processes applied to the single absorption type of plants. The study is further limited primarily to plants using elemental sulfur combustion as a source of sulfur dioxide although one plant burning sludge acid was studied.

This report compiles the available information that has been developed during the short operating history of dual adsorption plants that are located in the United States. The report also points out additional areas of needed information that should be obtained from future detailed experience data.

APPROACH

A data collection and analysis plan was employed to provide an analysis and definition of operations that have an influence on emissions under normal steady-state operations and under upset conditions. Data was gathered on the existing dual absorption plants and single absorption plants with SO_x scrubber systems that clean up vent gases from the exhaust stack of the acid plant. The data included periods of upset operations resulting from production equipment failures, process control instrumentation failures, electric power and water utility losses, start-up and shutdown operations, changes in sulfur quality and SO_2 feed conditions, and product concentration changes.

The four main sources of data and information were: (1) EPA survey of continuous monitoring records and studies, (2) acid manufacturing plant operator's log books, (3) designer-engineering consulting firms data and (4) acid plant equipment manufacturers performance data. Additional information was obtained from a technical literature search and in-house files. Contact was also made with independent researchers.

Five companies operating 12 acid plants were selected for visits. They are representative of the present sulfuric acid industry with typical sulfur-burning configurations using double absorption processes and single absorption plants with some type of sulfur oxide control equipment.

Plant selection criteria included the best available technology for emission reduction to meet the EPA new plant performance standards.

(1) Capacity should be representative of medium, or large commercial scale operation.

(2) Ability to achieve 99.7 per cent SO_2 removal efficiency without secondary pollution.

(3) Completeness of process control instrumentation at each plant equipped with stack emission monitoring equipment.

(4) Recognized leadership in pollution control system applications and a cooperative attitude in supplying reliable and complete data from both current and historical records.

(5) Application of state-of-the-art design to plants operating at full capacity without experimental design factors.

(6) Complete malfunction notations and failure diagnostics recorded on data logs and charts.

The inspection team consisted of two men. Standard data forms for efficient transcription of data into the data processing system were used where possible. Data were obtained directly from plant operations and by examination of existing data logs in their original form. Where possible, these log sheets were photocopied.

Five acid plant manufacutrers and designers of sulfuric acid production and control equipment were interviewed by Catalytic engineers. Process design and operation test data were collected where available to supplement data collected from all plant operators.

Data from completed EPA studies and test programs and current emission testing programs on sufluric acid plants were analyzed in addition to the data from plant operators and designers. EPA also provided plant operating data obtained from performance tests made to establish the compliance of sulfuric acid plants.

Computer programs were used for data reduction and statistical analysis to establish the effect of process parameters on emissions from the sulfuric acid plant.

An analysis was made of the important variables in the plant operation as they affected emissions from the process. The range of data was obtained during most the important expected off-normal, start-up, shutdown, and normal operations. The data was sorted and prepared for input to a multiple linear regression analysis program and standard statistical analysis. The result of the regression correlations and statistical analysis assisted in determining the significance of each of the variables in controlling the emissions. Process parameter variations were correlated with operating conditions and probable causes of off-normal operations.

SECTION IV

PROCESS DESCRIPTION

CONTACT SULFURIC ACID PROCESS

The basic contact sulfuric acid process was patented in England in 1831. Since this time continued improvement has refined the process to the present highly efficient operation. Although variations occur in the basic process resulting from differences in feed stock or application, all contact acid plants contain the same five basic operations. These basic operations are; (1) burning sulfur or sulfur bearing feed stocks to produce sulfur dioxide, (2) cooling the resulting SO_2 containing combustion gas, (3) catalytic oxidation of the SO_2 to SO_3, (4) cooling the resulting oxidized gas containing SO_3, (5) absorption of SO_3 in strong sulfuric acid.

The simplest contact plant results from use of elemental sulfur as feed stock. Where other feed stocks such as spent acid or acid sludge containing moisture and organics are used, additional processing steps must be added to remove the resulting water and particulate matter before processing the combustion products in the catalytic converter. Feed stock variation also affects the sulfur conversion ratio, the volume of exhaust gases, and the character and amount of pollution emitted. The processes discussed in this chapter all use elemental sulfur as feed stock.

More detailed process descriptions, material balances and equipment lists for all processes are included in Appendix A.

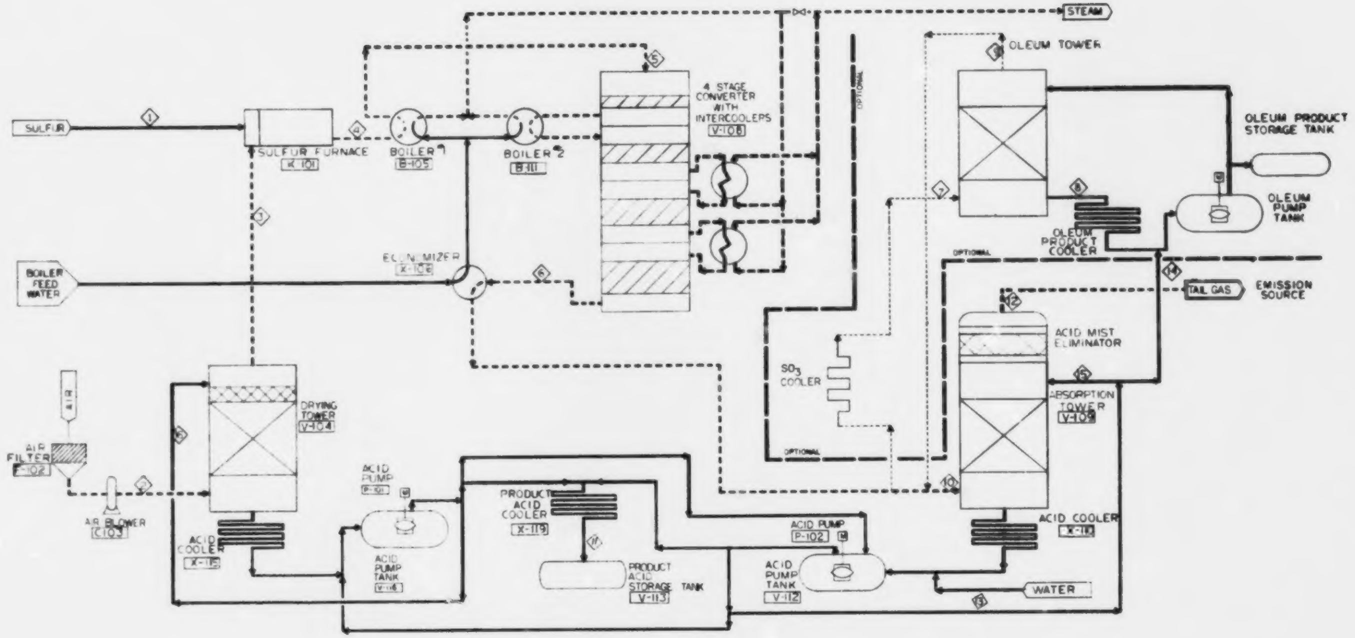
This appendix includes complete operating data for a typical single absorption acid plant taken from actual plant operation.

SINGLE ABSORPTION PROCESS

A simplified process flow diagram for a single absorption contact sulfuric acid plant burning elemental sulfur is presented in Figure 1.

In this process sulfur is burned with air to form a gas mixture containing approximately eight percent sulfur dioxide, 13 percent oxygen, and 79 percent nitrogen. Combustion air is pre-dried by passing it through a packed tower circulating 93 to 98 percent sulfuric acid. Pre-drying the air minimizes acid mist formation and resultant corrosion throughout the system.

Combustion products from the sulfur furnace pass through a boiler to cool the gas and generate process steam. The combustion products leaving the waste heat boiler contain sulfur dioxide and excess oxygen. These gases are passed through a multi-bed converter containing vanadium pentoxide catalyst that promotes the combination of sulfur dioxide and oxygen to produce sulfur trioxide (SO_3). The catalytic oxidation of SO_2 to SO_3 increases the temperature of the gas mixture in the catalytic converter. The heat generated in the first stages of catalytic oxidation must be removed to control the temperature for succeeding stages of conversion. This heat


SULFUR
1
SULFUR FURNACE
K-101
2
3
4
BOILER 1
B-105
BOILER 2
B-111
5
4 STAGE CONVERTER WITH INTERCOOLERS
V-108
ECONOMIZER
X-106
6
BOILER FEED WATER
STEAM
OPTIONAL
OLEUM TOWER
7
8
9
OLEUM PRODUCT COOLER
OLEUM PRODUCT STORAGE TANK
OLEUM PUMP TANK
SO3 COOLER
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OPTIONAL
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ACID PUMP TANK
V-112

SINGLE ABSORPTION
SULFUR BURNING CONTACT
SULFURIC ACID PLANT
PROCESS FLOW DIAGRAM

FIGURE 1

KEY	
GASES	------>
LIQUIDS	——→

is removed in additional waste heat boilers to generate process steam. Temperature of catalyst beds is also controlled by introduction of cold air into the converter. This is the air quench system. The temperature of the gases leaving the converter is approximately 806F to 815F with approximately 98 percent of the SO_2 converted to SO_3. These gases are then passed through an economizer to preheat the boiler feedwater going to the waste heat boilers.

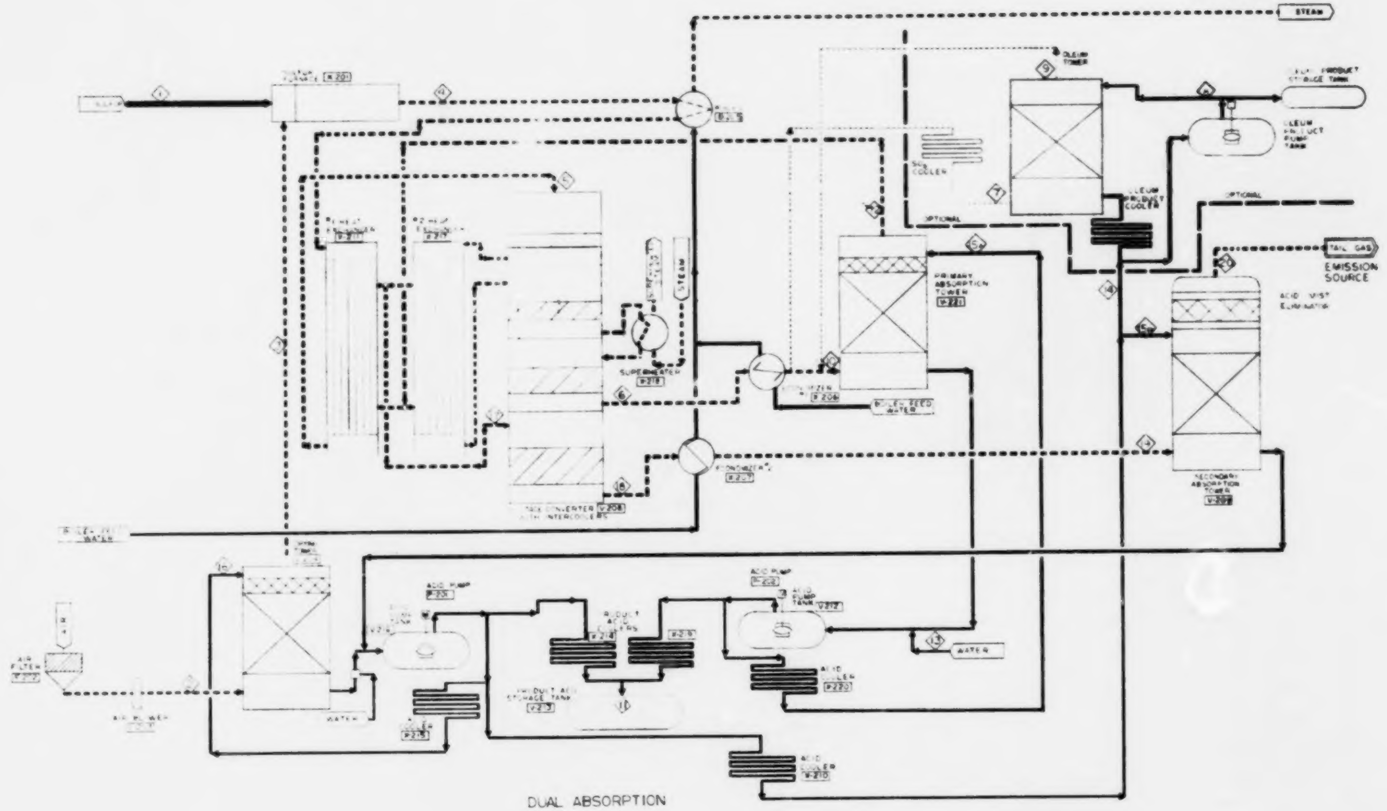
Sulfuric acid is produced by passing the gases leaving the economizer through an absorption tower where the SO_3 is absorbed in hot 98.5 to 99.0 percent sulfuric acid. In the absorption tower, sulfuric acid of desired strength is produced by controlling the acid concentration and water make-up and temperature of the feed acid. If fuming sulfuric acid or oleum is required, the gases containing SO_3 leaving the economizer are first passed through an oleum tower where SO_3 is dissolved in oleum to produce oleum. The gas stream leaving the oleum tower is further stripped of SO_3 by passing through a normal acid absorber containing 98.5 to 98.8 percent sulfuric acid. The majority of single absorption plants use a single absorption tower and produce a product acid with a concentration of 98 to 99 weight percent sulfuric acid.

A DUAL ABSORPTION PROCESS

The average single absorption sulfuric acid plant will produce SO_2 emissions in the range of 1600 ppm to 2000 volume ppm operating at normal efficiency. Since this emission level is in excess of the four pounds of SO_2 per ton of production allowed by the current standards, some modification of the single absorption process is required. The need for more efficient sulfuric acid plants initiated the development of the dual absorption plant The dual absorption process can convert 99.7 to 99.8 percent of the sulfur dioxide to sulfur trioxide for producing sulfuric acid.

A typical modern dual absorption plant burning elemental sulfur is shown in Figure 2. The primary difference between the single absorption and the dual absorption process is the addition of a primary SO_3 absorber for gas leaving the third catalyst bed. One process uses this absorber after the second bed. Since the addition of an absorber between catalyst beds requires cooling and reheating the process gas a change in the heat recovery system is also required.

Comparison of Figures No. 1 and 2 will show that the sulfur combustion portions of the single and dual absorption plants are similar. Combustion air is compressed and dried in a drying tower with 93 to 98 percent sulfuric acid before use for combustion of sulfur in the sulfur furnace. The hot gases from a sulfur furnace then pass through the waste heat boiler to generate process steam. The waste heat boiler is designed to permit further cooling of the combustion products to approximately 795 to 820F in the No. 1 heat exchanger by reheating part of the gas from the primary absorber. The cool gases are


SULFUR
SULFUR FURNACE F-201
BOILER B-215
STEAM
1st HEAT EXCHANGER E-211
2nd HEAT EXCHANGER E-217
SUPERHEATED STEAM
STEAM
SUPERHEATER E-218
TRAY CONVERTER WITH INTERCOOLERS V-208
ECONOMIZER #2 E-207
ECONOMIZER E-206
BOILER FEED WATER
SO3 COOLER
OPTIONAL
OLEUM TOWER
OLEUM PRODUCT COOLER
OLEUM PRODUCT STORAGE TANK
OLEUM PRODUCT PUMP TANK
PRIMARY ABSORPTION TOWER V-221
TAIL GAS
EMISSION SOURCE
ACID MIST ELIMINATOR
SECONDARY ABSORPTION TOWER V-209
BOILER FEED WATER
DRYING TOWER
AIR FILTER
AIR BLOWER
WATER
ACID PUMP P-201
ACID PUMP TANK V-214
ACID COOLER E-215
PRODUCT ACID COOLERS E-214 E-219
PRODUCT ACID STORAGE TANK V-213
ACID PUMP P-202
ACID PUMP TANK V-212
WATER
ACID COOLER E-220
ACID COOLER E-210
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
18
20
KEY
GASES
LIQUIDS

DUAL ABSORPTION

SULFUR BURNING CONTACT
SULFURIC ACID PLANT
PROCESS FLOW DIAGRAM

FIGURE 2

then passed through the first bed of the catalytic converter where the gas temperature is increased to approximately 1100 to 1130F. The high temperature gas exiting the first catalyst stage is cooled in No. 2 heat exchanger to approximately 820F for reaction in the second catalyst bed. The heat is used to reheat the remainder of the gas from the primary absorber. Heat generated in the second catalyst bed is removed by a steam superheater in the process steam line from the waste heat boiler. Heat generated in the third catalyst bed is removed by an economizer in the boiler feedwater system before the gas is fed to the primary absorption tower. In the primary absorption tower the concentration of SO_3 in the gas is reduced to about 100 ppm by contact with 98.5 percent sulfuric acid. Cold gas leaving the primary absorption tower must be reheated before introduction to the fourth catalyst bed. This is accomplished by passing in parallel through No. 1 and No. 2 heat exchangers.

Approximately 97 percent of the SO_2 remaining in the gas stream is converted to SO_3 in the fourth catalyst bed. This is a much high overall conversion rate than is possible in the single absorption plant. The increased conversion efficiency results from the lower partial pressure of SO_3 in the gas permitting the reaction to be driven more nearly to completion. The gases leaving the fourth absorption bed are finally cooled in a second economizer heating boiler feedwater before contacting 98.5 percent sulfuric acid in the secondary absorption tower. The gases leaving the secondary absorption tower will contain approximately 100 to 300 parts per million SO_2 under normal operations and will meet the existing emission standards without further processing.

If oleum is required, an oleum tower is inserted before the primary absorber in a manner similar to the single absorption process.

With the exception of the location of the primary absorber and heat exchangers previously discussed, all major designers of dual absorption sulfuric plants use the same basic equipment configuration. Important differences between these designs are found in the design details of the converter, heat exchangers and absorbers. Air quench is also used in some dual absorption plants.

SULFUR DIOXIDE RECOVERY PROCESSES

The typical single absorption contact sulfuric acid plant is not capable of meeting the current SO_2 emission standards using an economically feasible converter design. There is a lower limit to the concentration of SO_2 in the vent gas imposed by equilibrium conditions within the catalytic converter and the amount of catalyst that can be installed economically in the plant. Because of these limitations the single absorption sulfuric plant must be equipped with sulfur dioxide recovery processes to reduce the SO_2 concentration in the vent gas to the acceptable level.

Many processes have been proposed to perform this operation but only three have been applied commercially. These are the sodium scrubber process, the ammonia scrubber process, and the molecular sieve adsorption process. These three processes will be described in the following paragraphs.

Sodium Scrubber System

The sodium scrubber process for removing sulfur dioxide that was included in this study is a wet regenerative system based on a sodium sulfite/bisulfite cycle. This process, currently being marketed by Davy Powergas Inc. under the Wellman-Lord trademark, is represented by Figure 3 that depicts the absorber and chemical regeneration areas. The reactions that take place in the process can be simplified to the following:

Absorption - $SO_2 + Na_2SO_3 + H_2O \longrightarrow 2\ NaHSO_3$

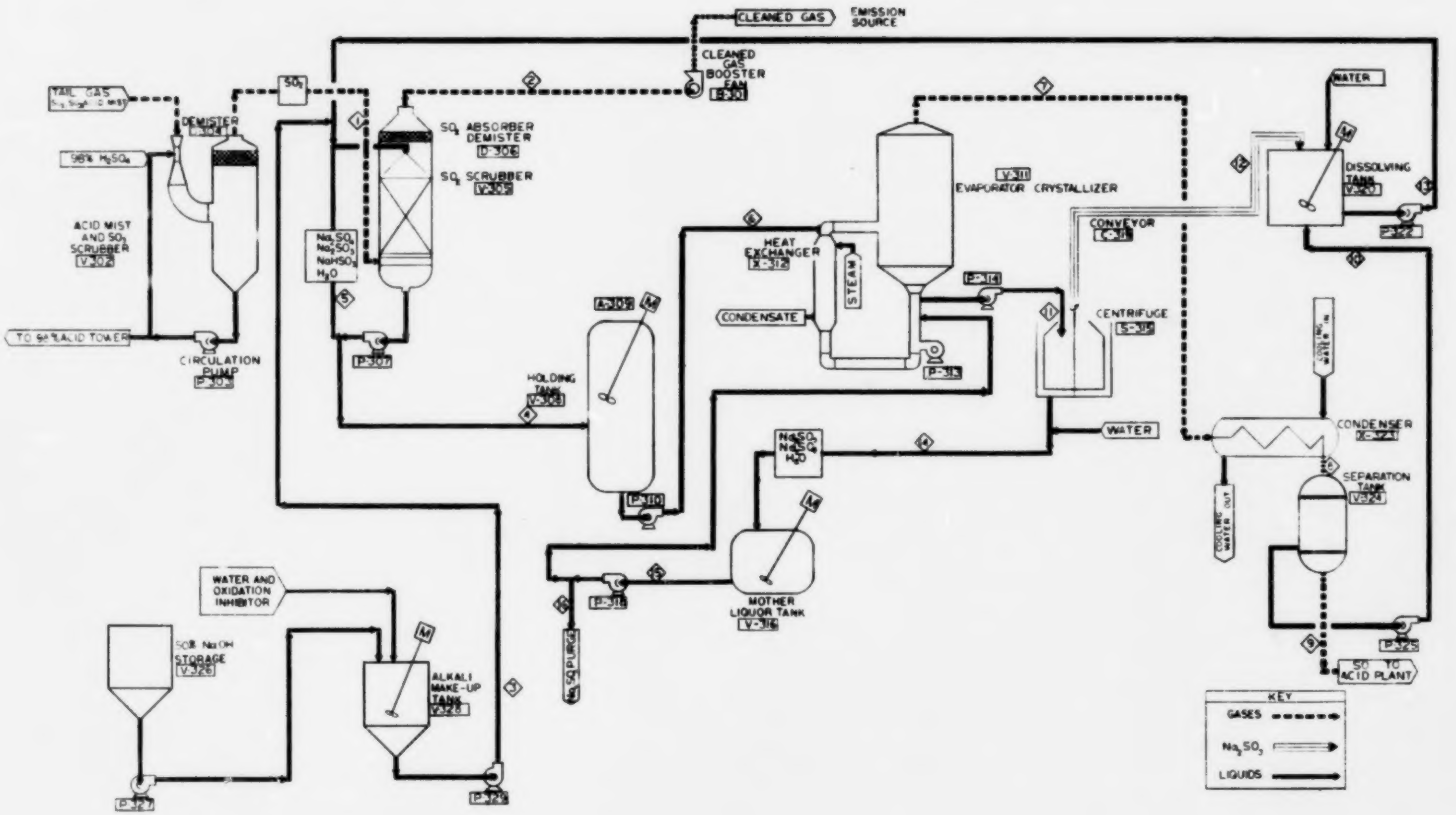
Regeneration - $2\ NaHSO_3 \longrightarrow Na_2SO_3 + SO_2 + H_2O$

Sodium sulfate (Na_2SO_4), which is non-regenerable in the normal process, is formed in the absorber as a result of the reaction between the sulfite ion and oxygen or sulfur trioxide as follows:

$Na_2SO_3 + 1/2O_2 \longrightarrow Na_2SO_4$

$2\ Na_2SO_3 + SO_3 + H_2O \longrightarrow Na_2SO_4 + NaHSO_3$

The sodium sulfate formed is controlled at a level of approximately five to ten percent by weight in the absorber feed stream by maintaining a continuous purge from the system. Caustic addition is required to replace the sodium lost in the sodium sulfate purge. This caustic make-up solution


TAIL GAS
98% H_2SO_4
ACID MIST AND SO_3 SCRUBBER
V-302
DEMISTER
TO 98% ACID TOWER
CIRCULATION PUMP
P-303
SO_3
1
SO_2 ABSORBER DEMISTER
D-306
SO_2 SCRUBBER
V-305
Na_2SO_4
Na_2SO_3
$NaHSO_3$
H_2O
5
P-307
2
CLEANED GAS
EMISSION SOURCE
CLEANED GAS BOOSTER FAN
B-301
HOLDING TANK
V-308
4
A-309
M
P-310
WATER AND OXIDATION INHIBITOR
50% NaOH STORAGE
V-326
P-327
ALKALI MAKE-UP TANK
V-328
3
P-329
Na_2SO_4 PURGE
P-318
MOTHER LIQUOR TANK
V-316
6
HEAT EXCHANGER
X-312
STEAM
CONDENSATE
P-313
V-311
EVAPORATOR CRYSTALLIZER
7
P-314
11
CENTRIFUGE
S-315
CONVEYOR
C-319
WATER
14
12
DISSOLVING TANK
V-320
13
P-322
COOLING WATER IN
COOLING WATER OUT
CONDENSER
X-323
8
SEPARATION TANK
V-324
9
P-325
SO_2 TO ACID PLANT
KEY
GASES
Na_2SO_3
LIQUIDS

SODIUM SCRUBBER

TAIL GAS CLEANING SYSTEM
PROCESS FLOW DIAGRAM

FIGURE 3

reacts with the sodium bisulfite in the absorber to form additional sodium sulfite solution:

$NaOH + NaHSO_3 \dashrightarrow Na_2SO_3 + H_2O$

The caustic can also react with the SO_2 to form bisulfite as follows:

$NaOH + SO_2 \dashrightarrow NaHSO_3$

The SO_2-rich gas is contacted counter-currently in the absorber by the sodium sulfite solution and passes out the top stripped of SO_2. An absorber with inlet concentration of 1560 parts per million SO_2 and 95 percent scrubber efficiency can achieve an emission of 86 parts per million SO_2. The absorber bleed stream, rich in sodium bisulfite, ($NaHSO_3$), is discharged to a holding tank. From the holding tank the solution flows to the chemical regeneration area for recovery of the SO_2 gas.

The sodium bisulfite solution flows to the evaporator crystallizer in the chemical regeneration area where it is boiled by indirect heating with steam, resulting in the decomposition of the sodium bisulfite solution into SO_2, water vapor, and a precipitate of sodium sulfite crystals.

The overhead gas from the evaporator-crystallizer passes through a condenser to remove most of the water vapor. Condensate is recycled to the dissolving tank to dissolve the sodium sulfite crystals and the product SO_2 gas is recycled to the sulfuric acid plant or Claus elemental sulfur plant. Precipitate from the evaporator-crystallizer is processed through a centrifuge where sodium sulfite solids are discharged to a dissolving tank for recycle to the absorber. The bulk of the mother liquor from the centrifuge is recycled to the evaporator-crystallizer for solids density control. A small portion of the mother liquor is purged from the process to control the level of sodium sulfate as previously stated. The sodium ions lost in the purge stream are replaced by addition of sodium hydroxide (50 percent NaOH) solution directly to the absorber.

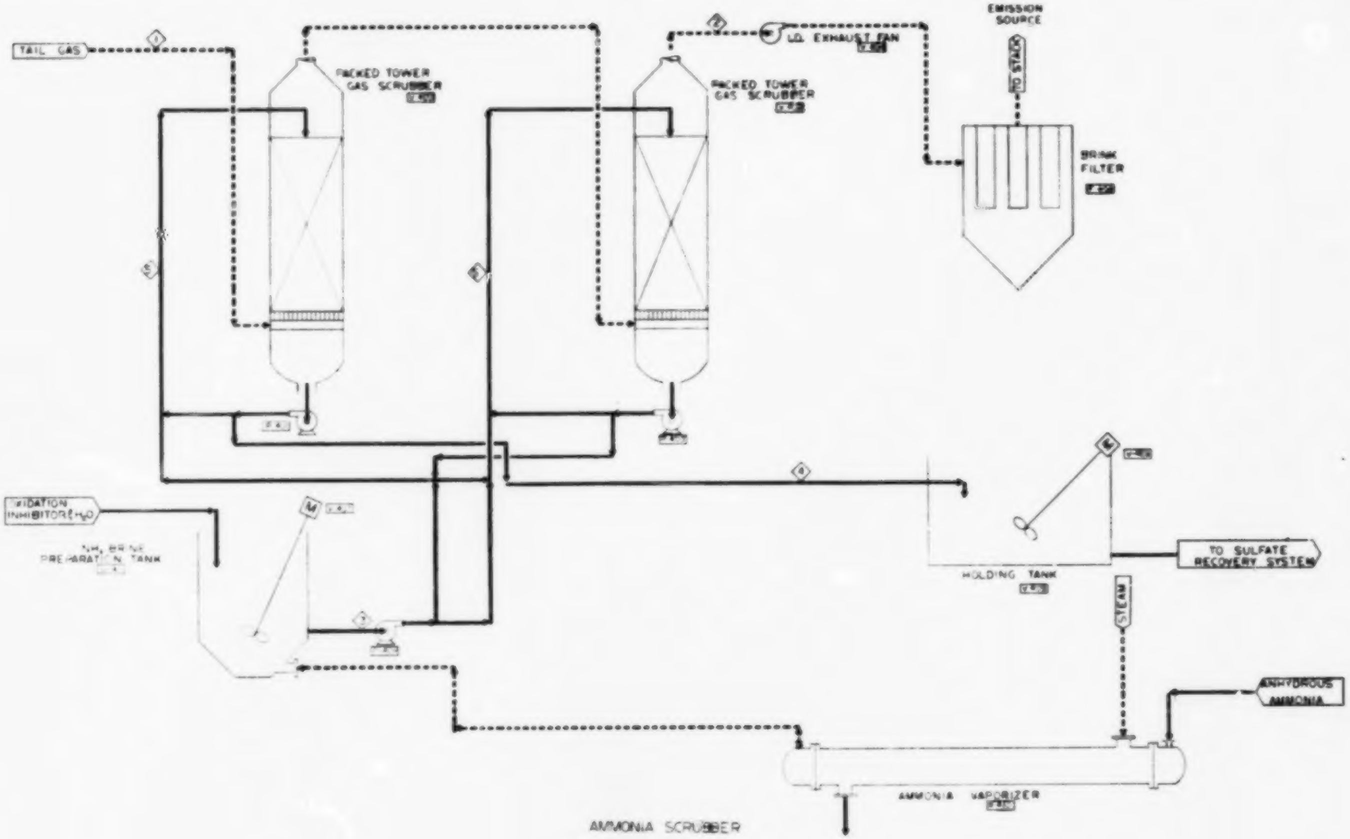
Ammonia Scrubber Process

Ammonia has been used for removing sulfur dioxide from vent gases in the sulfuric acid and smelter industries for many years. Several commercial ammonia scrubber processes are available for application to sulfuric acid plants. All of these processes are based upon the same chemical reactions. A flowsheet of this process is shown in Figure 4.

Ammonia provides one of the most vigorous reactions with sulfur dioxide of all the alkaline materials and produces soluble by-products. The primary reaction in the ammonia scrubber is the conversion of ammonium sulfite to ammonium bisulfite by the reaction with sulfur dioxide. The ammonium bisulfite is regenerated by reaction with ammonia to again form ammonium sulfite. The equations for the two reactions are as follows:

$SO_2 + (NH_4)_2SO_3 + H_2O \dashrightarrow 2NH_4HSO_3$

$NH_3 + NH_4HSO_3 \dashrightarrow (NH_4)_2 SO_3$


TAIL GAS
1
PACKED TOWER GAS SCRUBBER
PACKED TOWER GAS SCRUBBER
2
I.D. EXHAUST FAN
EMISSION SOURCE
TO STACK
BRINK FILTER
4
OXIDATION INHIBITOR & H_2O
NH_3 BRINE PREPARATION TANK
M
M
HOLDING TANK
TO SULFATE RECOVERY SYSTEM
STEAM
ANHYDROUS AMMONIA
AMMONIA VAPORIZER

AMMONIA SCRUBBER

TAIL GAS CLEANING SYSTEM
PROCESS FLOW DIAGRAM

FIGURE 4

In applying the ammonia scrubbing system to a sulfuric acid plant exhaust gas, the gas is first treated by spraying water into the exhaust duct to humidify and cool the gases leaving the absorber. The cool gases are then passed through an absorber counter current to the flow of the ammonia brine and the SO_2 removed by reaction with ammonium sulfite. The concentration of ammonia sulfite is controlled by the addition of ammonia on the basis of pH. Operation with a large concentration of ammonium sulfite promotes the reaction with SO_2 but increases the usage of ammonia since a large amount of ammonium sulfite is withdrawn with the spent scrubber liquor. Operation with a large concentration of ammonium bisulfite reduces the absorption capability of the brine and increases the concentration of SO_2 leaving the absorber. Careful control of the pH of scrubbing liquor is required for efficient operation of the system.

A secondary reaction taking place in the absorber is the oxidation of the ammonium sulfite to ammonium sulfate by reaction with excess oxygen in the exhaust gas stream. The chemical equation for this oxidation process is as follows:

$(NH_4)_2SO_3 + 1/2\ O_2$ ---- $(NH_4)_2SO_4$.

The oxidation of ammonium sulfite to sulfate is undesirable since ammonium sulfate is unreactive in the scrubbing mechanism and removes ammonia from the system in the largest ratio to the sulfur content.

The top of the absorber is equipped with a mist entrainment separator to prevent the carry over of ammonia brine in the gas stream. This separator is usually of the wire mesh type.

The primary disadvantage of removing SO_2 by absorption with ammonia brine is the generation of particulate matter by gas phase reaction between SO_2 and ammonia to form ammonium sulfite. The ammonium bisulfite particulate is very finely divided and passes through the absorber and is visible in the vent gas as a blue haze. The quantity of haze produced depends upon the partial pressures of the various gases in the vapor phase and cannot be completely eliminated using pH control in a single stage absorption. Where the particulate haze is not permissible in the exhaust gas from sulfuric acid plants, it has been standard practice to equip the plant with a venturi scrubber or a fiber pad demister operating at very high efficiencies to remove the submicron particulate. Although these high efficiency filters are satsifactory for removal of the particulates, the high pressure drop across the filters requires a large investment in additional blower capacity and energy consumption. Similar costs are encountered using a high energy venturi scrubber for removal of the particulate.

Various processes have been developed for reclaiming the sulfur values from the ammoniacal brine withdrawn from the absorber processes. These include acidulation with sulfuric acid, thermal decomposition of the ammonium bisulfite to sulfite and SO_2, and mixing of the ammonium sulfite-bisulfite liquor into fertilizer solutions. The thermal decomposition process is still in pilot plant development by TVA and was not applied commercially in any of the plants studied.

In the acidulation process, the ammoniacal brine from the absorber is mixed with sulfuric acid before being admitted to a packed column. In this column the reaction of sulfuric acid with ammonium sulfite-bisulfite takes place, liberating gaseous SO_2 and generating ammonium sulfate. The primary reactions in the acidulation process are shown in the following equations.

$$(NH_4)_2SO_3 + H_2SO_4 \dashrightarrow (NH_4)_2SO_4 + H_2O + SO_2$$

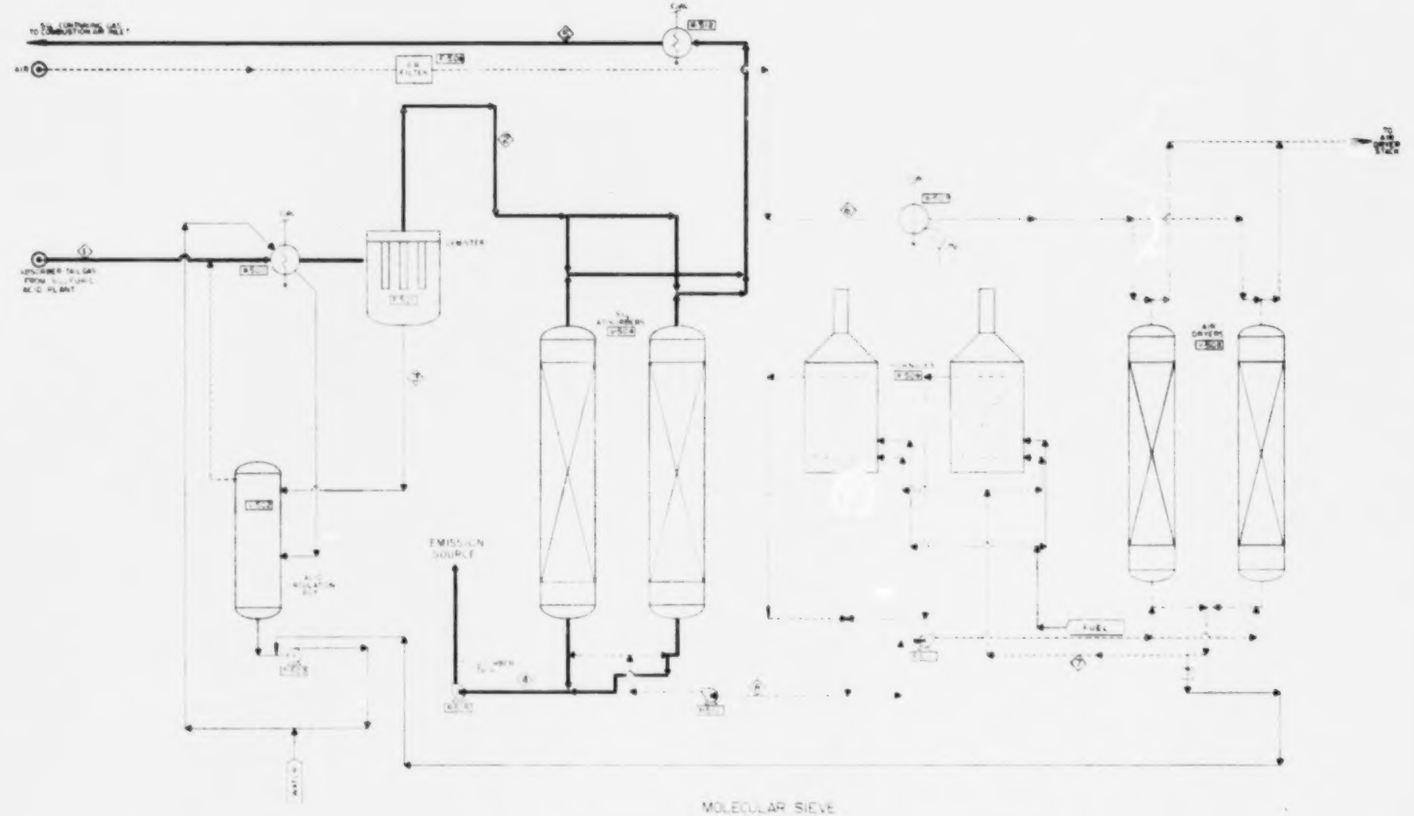
$$2\ NH_4HSO_3 + H_2SO_4 \dashrightarrow (NH_4)_2SO_4 + 2H_2O + 2\ SO_2$$

The packed column disengages the gaseous SO_2 from the ammonium sulfate solution so the SO_2 can be recycled back to the sulfuric acid plant while the ammonium sulfate solution is collected for further processing. The ammonium sulfate solution is either concentrated and crystallized to produce solid ammonium sulfate or is included in mixed fertilizers. When the acid plant is a part of a fertilizer complex, the ammonium sulfate or ammonium sulfite-bisulfite brine can be used in the diammonium phosphate production process as was the case in Plant "U" included in the study. The brine can also be used in other fertilizer concentrates using standard processes for manufacturing solid or fluid products.

Molecular Sieve Adsorption Process

One of the newest SO_2 recovery processes to be applied commercially to sulfuric acid plant vent gas is the PuraSiv S process development by Union Carbide. This process uses a dry bed molecular sieve material for removing SO_2 from the vent gas. The primary features incorporated in this system are the high removal efficiency for SO_2 especially at low SO_2 concentrations, freedom from liquid chemical handling problems, absence of waste products, and simple operation. Evaluation tests on production models of this system have been run very recently and data could not be fully evaluated in this study. However, general process descriptions are included because of the prospects of future applications.

A process flow diagram for the molecular sieve sulfur dioxide recovery system is shown in Figure 5. The tailgas from the sulfuric acid plant at approximately 170F is cooled to 100F by passing through a water cooler. Any sulfuric acid entrained from the absorption tower is collected from this cooler in an acid circulation pot. Acid from the circulation pot is continuously recycled to the cooler to aid in condensation and collection of the sulfuric acid mist. Since it is undesirable for liquid sulfuric acid to enter the molecular sieve adsorption tower, the gas is passed through a filter containing packed fiber elements to remove entrained sulfuric acid. The sulfuric acid collected in this filter is also



TO COMBUSTION AIR INLET
AIR
FILTER
AIR
DEMISTER
ABSORBER TAIL GAS
FROM SULFURIC
ACID PLANT
EMISSION
SOURCE
FUEL
AIR
DRYERS
TO
AIR
DRYER
STACK
1
2
7

MOLECULAR SIEVE

TAIL GAS CLEANING SYSTEM
PROCESS FLOW DIAGRAM
FIGURE 5

returned to the acid circulation pot. This feed preparation system for the PuraSiv operation is similar to that included in many sulfuric acid plants to reduce the amount of sulfuric acid entrainment from the absorber system.

After removal of all excess sulfuric acid mist from the gas stream the gases are passed through a tower packed with granular PuraSiv S. In this tower the SO_2 is removed from the vent gas to a level of 15 to 20 parts per million. The molecular sieve adsorption system consists of two adsorber towers to permit regeneration of one tower while the second is being used to adsorb SO_2.

When the molecular sieve in one adsorption tower nears saturation, as indicated by an increase in the sulfur dioxide concentration in the vent gas, the towers are switched and the saturated tower is put on the regeneration cycle. Regeneration of the PuraSiv S is accomplished by passing a hot, dry air stream through the bed in reverse direction to strip out the adsorbed SO_2.

Regeneration air is brought into the plant through an air filter and a water cooled indirect cooler to remove as much of the water vapor as possible. The air is then passed through a desiccant bed dryer to remove the remaining moisture before being preheated to 200F in indirect fired air heaters. The air is then used for stripping the SO_2 in the regeneration cycle. Stripping air leaving the regenerating adsorber flows to the acid plant for mixing with dilution air in the sulfur furnace. This air contains from four to 0.3 percent SO_2 depending upon the point in the regeneration cycle. In this manner the recovered SO_2 is returned to the sulfuric acid plant converter for recovery as sulfuric acid.

To provide an uninterrupted flow of regeneration air two desiccant towers are used for air drying. As in the SO_2 adsorption towers, one tower is on adsorption cycle while the second is being regenerated. Regeneration is accomplished by passing the dried hot air from the fired air preheaters through the desiccant bed in reverse direction to strip out the adsorbed water which is then vented to atmosphere.

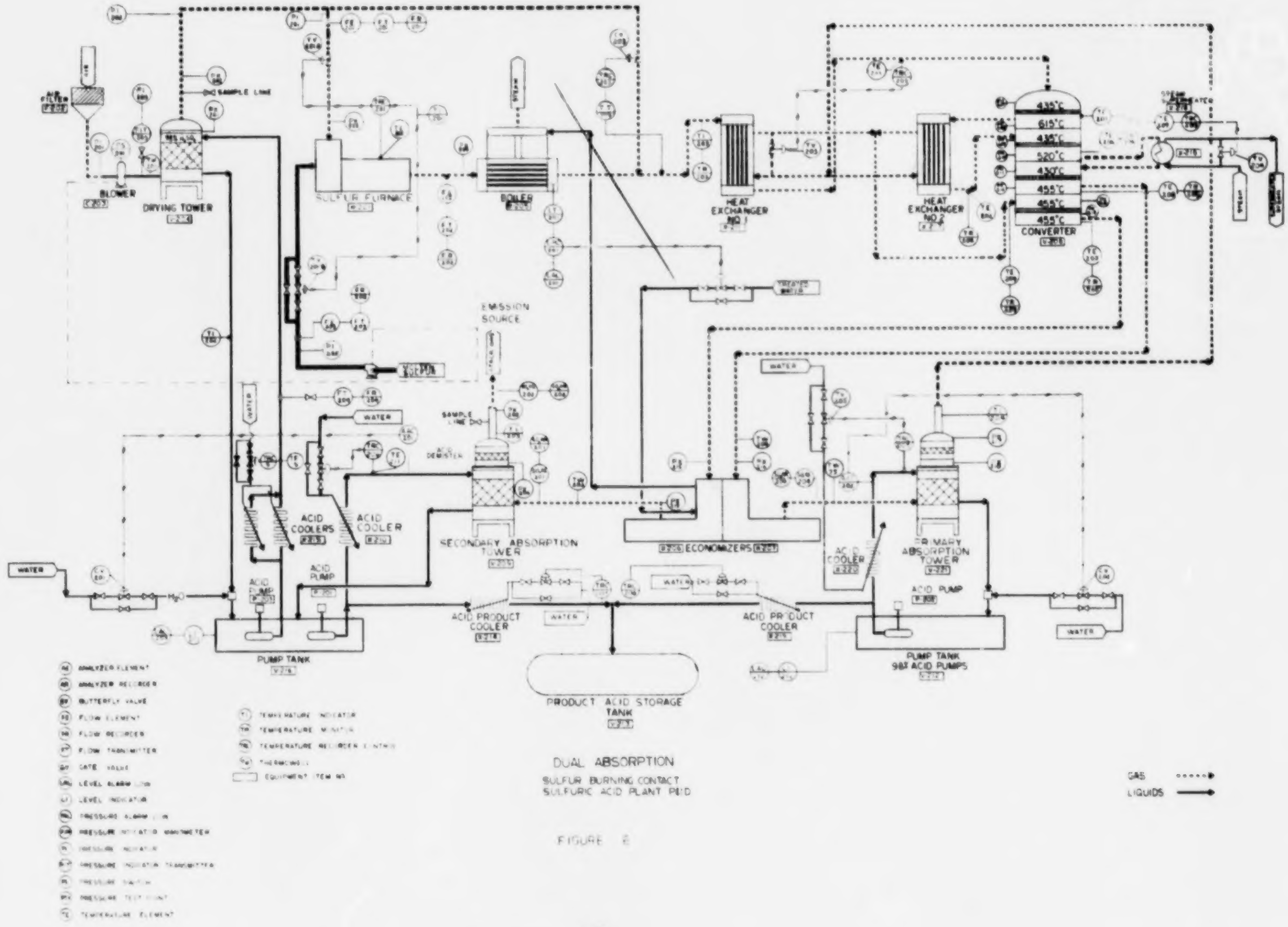
A control system is provided to determine the point when regeneration of both the SO_2 adsorber and the dryer is required and to automatically cycle the units to place a newly regenerated tower into operation. In this manner there is no interruption of either process or regenerating air flow. The regeneration air flow required in the SO_2 absorber is approximately 20 percent of the design process flow. Since about the same percentage of the total air flow is required for regeneration of the air dryers, the air drying units are small compared to the SO_2 adsorbers.

The SO_2 content of the recycled stripping air varies from four to 0.3 percent SO_2 throughout the regeneration cycle. The addition of this SO_2 to the SO_2 concentration leaving the furnace will vary the SO_2 concentration entering the converter also. During normal operation this variation of SO_2 entering the converter does not adversely affect the operation of the sulfuric acid process. Also, since the adsorption efficiency of the PuraSiv S is not highly dependent upon flow rate or concentration of SO_2, normal upsets in acid plant operation do not affect the concentration of SO_2 in the vent gas from the PuraSiv S system. It has also been found that the presence of CO_2 and NO_x in the vent gas as a result of burning acid sludges or dirty sulfur do not affect the adsorption efficiency of the PuraSiv S system.

Instrumentation and Control

Each manufacturer of sulfuric acid plants includes variations in the instrumentation control systems as well as variations in equipment and equipment arrangements. Although different instruments and controls are included, certain process parameters are either controlled automatically or recorded to permit manual control in all acid plants.

The most important instruments and controls are shown in the process and instrument diagram of Figure 6. This diagram shows a typical dual absorption acid plant as previously described. The most important process parameters are those affecting the temperatures and sulfur dioxide concentrations in the converter, and the sulfur trioxide concentrations and temperature of acid in the absorbers. All of these process parameters directly affect the emissions of SO_2 and acid mist


AIR FILTER
BLOWER
DRYING TOWER
SAMPLE LINE
SULFUR FURNACE
STEAM
BOILER
HEAT EXCHANGER NO 1
HEAT EXCHANGER NO 2
435°C
615°C
435°C
520°C
430°C
455°C
455°C
455°C
CONVERTER
STEAM SUPERHEATER
TREATED WATER
EMISSION SOURCE
SAMPLE LINE
ACID DEMISTER
WATER
H_2O
ACID COOLERS
ACID COOLER
ACID PUMP
SECONDARY ABSORPTION TOWER
ECONOMIZERS
PRIMARY ABSORPTION TOWER
ACID PRODUCT COOLER
PUMP TANK
PUMP TANK 98% ACID PUMPS
PRODUCT ACID STORAGE TANK
ANALYZER ELEMENT
ANALYZER RECORDER
BUTTERFLY VALVE
FLOW ELEMENT
FLOW RECORDER
FLOW TRANSMITTER
GATE VALVE
LEVEL ALARM LOW
LEVEL INDICATOR
PRESSURE ALARM LOW
PRESSURE INDICATOR MANOMETER
PRESSURE INDICATOR
PRESSURE INDICATOR TRANSMITTER
PRESSURE SWITCH
PRESSURE TEST POINT
TEMPERATURE ELEMENT
TEMPERATURE INDICATOR
TEMPERATURE MONITOR
TEMPERATURE RECORDER CONTROL
THERMOWELL
EQUIPMENT ITEM NO
GAS
LIQUIDS

DUAL ABSORPTION

SULFUR BURNING CONTACT
SULFURIC ACID PLANT P&ID

FIGURE 6

from the unit.

The sulfuric acid production rate is controlled by regulating the flow of molten sulfur and air to the sulfur furnace. These flows are properly ratioed and controlled by the temperature of the gas leaving the furnace. The SO_2 concentration in this gas is higher than required for the converter feed, so the gas is diluted by addition of dry air controlled by a temperature controller on the feed to the converter. This reduces the SO_2 concentration in the feed gas to the first stage of the catalytic converter. The inlet temperature to the converter must be precisely controlled for optimum conversion of SO_2 to SO_3. Additional temperature control is obtained in the feed stream by regulating the amount of cold gases from the primary absorber flowing to the No. 1 heat exchanger. Since the waste heat boiler must be operated to provide sufficient steam for driving the turbine on the primary blower, the balance in heat transfer between the No. 1 and No. 2 exchanger must be adjusted manually with by-pass valves to properly set the range of heat transfer in the No. 1 heat exchanger and heat recovery boiler.

These by-pass valves and others around heat exchanger No. 2, also are used to adjust the temperature distribution in the various stages of the catalytic converter. For proper conversion of SO_2 to SO_3, inlet and outlet temperatures of each stage must be carefully controlled within a narrow range. Control and adjustment of the converter temperatures is provided by a multi-point temperature recorder recording the inlet and outlet temperatures on each catalyst section. Observation of the temperature profile across the converter will permit quick analysis of the status of the conversion efficiency of the unit. This multi-point temperature recorder is the heart of the control system for the sulfuric acid plant.

Critical parameters around the primary absorber are the temperature, flow, and concentration of the acid feed to the absorber. If these parameters are outside the acceptable range, acid mist is generated in the absorber and is discharged from the plant vent. Temperature of the absorbing acid is controlled by adjusting the water flow on the inlet acid cooler while the concentration of acid is adjusted by a concentration analyzer controlling the amount of water make-up to the strong acid exiting the absorber. The same process parameters are as important on the secondary absorber as on the primary unit, and must be controlled as well.

Since the dual absorption plant was designed for the purpose of reducing the SO_2 and acid mist emissions from the plant, as well as increasing the efficiency of acid manufacturing, the important measurement of the success of operation of the plant is the SO_2 analyzer installed in the vent gas stack. This automatic analytical instrument continuously monitors the SO_2 concentration in the vent gas, indicating when one of the process variables exceeds optimum range of operation. When an excessive concentration of SO_2 in the stack exists, the instrumentation including the multi-point recorder on the converter, is used to diagnose the problem and correct the emissions.

Many other instrument and control systems are required for proper operation of a sulfuric acid plant. These include instruments on such auxiliaries as the waste heat boiler, economizer, concentrated acid sumps, boiler feedwater for economizers and boiler, the air drying tower, and storage units. Although these instruments are important to operation of the plant, their effect on the emissions of the plant are not as direct as those previously discussed. Most of the data collected in our plant survey and presented in the next section include the important process parameters discussed in the first portion of this section and are analyzed in the succeeding section.

SECTION V

SURVEY OF ACID PLANT EMISSIONS AND CONTROLS

SELECTION OF PLANTS FOR FIELD SURVEYS

The primary purpose of this study was to obtain information showing the relationship between acid plant process variables and emissions. The study was concerned with those plants that could meet the air pollution control standards under normal operation. Reporting only those plants that will meet air pollution control standards limits the study primarily to dual absorption acid plants and those single absorption plants equipped with vent gas cleaning systems. Three vent gas cleaning systems were selected as being properly proven in commercial installations. These were the sodium scrubbing system, the ammonia scrubbing system, and the Union Carbide PuraSiv system.

The application of the dual absorption process is relatively new in this country and only a limited number of these plants are in operation. Vent gas cleaning systems are also relatively new in commercial application, limiting the number of plants available from which information could be obtained. Because of the limited number of dual absorption plants available for study, comparative information from several single absorption plants was included in the study to support information obtained from dual absorption plants. Many process variables can be correlated between the two plants since process variables have similar effect on emissions in both.

The newest gas cleaning system applied commercially is the Union Carbide PuraSiv system. Only one plant is operating commercially with sufficient experience to provide operating data. This plant was not available for a visit because of the proprietary nature of the process but data was obtained from the performance test performed by EPA.(3)

After a review of the industry a list of tentative plants was prepared (See Table 1) including all the known dual absorption plants and examples of the three major gas cleaning processes. A list of acid plant design companies was also compiled as a possible alternate source of acid plant operating information. Visits to several of the major plant design firms produced very little useful data because they considered their plant designs as proprietary to themselves and performance test data from plants that they installed as proprietary to the clients. After this initial effort attention was turned to obtaining data from operating plants.

All of the candidate sulfuric acid plants were investigated and five companies were selected for visits. The selection was based upon the appropriateness of plant type and willingness to provide the required information on the operation of the plants. The EPA task officer approved the list of selected plants to be visited.

During the field visits to the selected locations, contractor personnel examined a total of 12 contact acid plants.

TABLE 1

A LIST OF CANDIDATE COMPANIES FOR THE SULFURIC ACID PLANT MALFUNCTIONS EMISSIONS SURVEY

Single W/NH_3 Scrubbing		Single W/Na Scrubbing		Dual Absorption on Line		New Dual Absorption Start-Up	
No. of Plants	Company	No. of Plants	Company	No. of Plants	Company	No. of Plants	Company
(2)	C. F. Industries	(1)	Olin, Inc.	(1)	American Cyanamid	(1)	Freeport Chem.
(1)	Conserve, Inc.	(1)	Olin, Inc.	(1)	Miss. Chemical	(1)	Agricultural Prod.
(2)	Olin, Inc.	(1)	Allied Chemical	(1)	N. L. Industries	(1)	Texasgulf
(1)	Collier Carbon & Chemical Company			(1)	Stauffer Chemical	(1)	N. L. Industries
(1)	Allied Chemical Co.			(1)	Standard Oil of Cal.	(1)	Allied Chemical
(1)	W. R. Grace			(1)	American Smelting and Refining Co.	(2)	C. F. Industries
(2)	Texas Gulf					(1)	Miss. Chemical
						(2)	Agrico
						(3)	IMC

The location and type of plants visited are listed below:

No. of Plants Surveyed	Type of Contact Acid Plant	Location
2	Single Absorption without Tail Gas Cleanup	North Carolina
4	Single Absorption with Ammonia Scrubber	Florida
3	Single Absorption with Sodium Scrubber	Maryland
3	Dual Absorption	(1) Florida (1) North Carolina (1) Texas

12 - Total number of plants surveyed at the five (5) locations

TYPE OF EMISSION CONTROL SYSTEMS

The acid plants visited are listed in Table 2 using letter codes to protect the confidentiality of the plant data. This table indicates the types of emission control systems found at each plant. The information on plants "A" and "X" was furnished from EPA records as these two plants were not available for inspection. The data furnished on these two plants are helpful in this study even though the plants could not be visited.

The two (2) single absorption plants (M_1,M_2) located in North Carolina have no tail gas cleaning systems. The single absorption plants (K, T, U_1, U_2) visited in Florida had ammonia scrubbing systems for tail gas cleanup. Plant "U_1", also uses a mist eliminator on the downstream side of the ammonia scrubber.

TABLE 2

SUMMARY OF EMISSIONS FROM VARIOUS TYPES OF CONTACT SULFURIC ACID PLANTS SURVEYED DURING NORMAL OPERATIONS

Code Letters	Q	M_1	M_2	H
Type of Sulfur	Bright Sulfur	Bright Sulfur	Dark Sulfur	Dark Sulfur
Type of Plant	Dual	Single	Single	Dual
H_2SO_4 (100%) Production Rate, tons/day	1600-1650	1565	1565	1500-1800
Conversion Efficiency Percent	99.7-99.9	97.14	95.6%	99.75-99.85
Stack Gas Rate, scfm x 10^3	96-106.6			85-105
SO_2 Entering Converter Vol. %	8.6-8.9	7.0-8.0	7.0-8.0	9.0
SO_2 Removal Eff. %	99.7	98.0	98.0	99.7
SO_2 Emitted, ppm by Vol.	101-134	2500	1300-3300	40-300
lb. per Ton	1.17-2.04	33.5	17.4-44.2	1.0-4.0
lb./scf x 10^{-5}	1.60-2.48			1.0-3.0
SO_3 Emitted, mgSO_3/scf		0.56-6.15	1.0-30.55	
Vol. % SO_3	0.00009	.0004-.0059	0.17-0.30	
ppm (vol.) SO_3	0.9 ppm	4-59	1700-3000	
Mist H_2SO_4 Emitted lb./ton Acid	0.037-0.955		0.03-0.06	
H_2SO_4 Mist Removal Efficiency	99.5+	98.3	99.9	97.7
mg/scf	0.15-06-.03			
Average SO_2, mg/scf	0.88			
Average SO_3, mg/scf	0.65			
Opacity %	0	5-10	20-80	0
Local Standard SO_2 (new)	N. Carolina 27#/T	N. Carolina 27#/T	N. Carolina 27#/T	Florida 10#/T

TABLE 2 (continued)

SUMMARY OF EMISSIONS FROM VARIOUS TYPES OF CONTACT SULFURIC ACID PLANTS SURVEYED DURING NORMAL CONDITONS

Code Letters	A	X	Y	J (1)
Type of Sulfur	Bright Sulfur	Bright & Dark	Sludge Acid & Sulfur	Copper Ore Roaster SO_2
Type of Plant	Dual	Single	Single with sodium scrubbing	Dual
H_2SO_4 (100%) Production Rate, tons/day	1500-1510	1100-1150	1000	500
Conversion Efficiency Percent	99.00-99.9	97.6-98.0	98.0	92.7-99.9
Stack Gas Rate, scmf x 10^3		74.3		100.0
SO_2 Entering Converter Vol. %	9.3-9.4	8.0	8.0	2-19
SO_2 Removal Eff. %	99.7	97.9	90-92	99.7
SO_2 Emitted, ppm by Vol.	170-400	1600	30-200	0.03-3110.2
lb. per ton		34.96		
lb./scf x 10^{-5}				
SO_3 Emitted, mgSO_3/scf			.200-.224	
Vol. % SO_3				
ppm (vol.) SO_3				
Mist H_2SO_4 Emitted lb./ton Acid			.068-.087	
H_2SO_4 Mist Removal Efficiency %		99.5+	99.5	
mg/scf				
Average SO_2, mg/scf				
Average SO_3 mg/scf				
Opacity %	10	3.10		
Local Standard SO_2 (new)	Mississippi 500 ppm (n) 2000 ppm (e)	Florida 10#	Maryland 2000 ppm	Texas 25#/T

(1) DAP feed from smelter.

TABLE 2 (Continued)

SUMMARY OF EMISSIONS FROM VARIOUS TYPES OF CONTACT SULFURIC ACID PLANTS SURVEYED DURING NORMAL OPERATIONS

Code Letters	U_2	U_1	K	T
Type of Sulfur	Dark Sulfur	Dark Sulfur	Bright Sulfur	Sulfur Single with Ammsox
Type of Plant	Single with ammonia scrubber & mist elim.	Single with Ammonia scrubbing. No mist eliminator.	Single with ammonia scrubbing	Single with Ammonia scrubbing
H_2SO_4 (100%) Production Rate, tons/day	1000	1000	1300	1000
Conversion Efficiency Percent	96.6-98.3	98.0	98.99	63.0
Stack Gas Rate, scfm x 10^3	57.6	86.4	83.4	63
SO_2 Entering Converter Vol. %	8.4	6.45-8.80	8.0	7.5
SO_2 Removal Eff. %	98.3	98.3	98.0	98.0
SO_2 Emitted, ppm by Vol.	482-509	910-1900	500-1000	2100-2200
lbs/ per ton	16.4	12.2-25.4	2.554	10-33
lb./scf x 10^{-5}		1.43-3.00		
SO_3 Emitted, mgSO_3/scf				5-10
Vol. % SO_3				
ppm (vol.) SO_3				
Mist H_2SO_4 Emitted lb./ton Acid				2.0
H_2SO_4 Mist Removal Efficiency	98.0	90.0	99.5+	99.5
mg/scf				
Average SO_2, mg/scf				
Average SO_3, mg/scf				
Opacity %	O-Brink		5-20	O-Brink
Local Standard SO_2 (new)	Florida 10/#	Florida 10/#	Florida 10/#	Florida 10/#

The single absorption plants located in Maryland ("Y") use sodium scrubbing systems. The process descriptions of the ammonia scrubbing system and the sodium scrubbing system are found in Section IV, "Process Description".

In the dual absorption plants (A,H,Q,J) the SO_2 emission control is inherent in the process itself. Control of acid mist emissions is accomplished through mist elimination devices incorporated in plant design. Section IV has further information on the emission control system found in the dual absorption plants.

EMISSIONS DATA OBTAINED

The emissions and operating data obtained during this study were supplied by most of the major sulfuric acid manufacturers that are located in the United States. Emissions data was received from more than 65 percent of the new dual absorption plants that were started up during 1974.

Table 2 shows operating data and emissions data from all plants visited by the contractor plus data on two plants (A,X) not visited by the contractor. Production rates are shown for each plant and the SO_2 emitted is shown in pounds of SO_2 per ton of 100 percent H_2SO_4 produced. The acid mist emitted is listed in terms of pounds of (100 percent) H_2SO_4 mist per ton of 100 percent H_2SO_4 produced. The data in Table 2 were recorded during steady-state operations and serves as a basis for comparison to data obtained during upsets.

Table 3 lists data that were recorded at a dual absorption acid plant during a new source performance standards test conducted in 1974. This test was observed by EPA personnel and all emissions were well below the EPA standard.

Figure 7 shows the relationship between the EPA standard emission limit for SO_2 expressed as "pound per ton of 100 percent acid produced" and "parts per million by volume" in the stack gas for various SO_2 concentration inlet to the converter. The standard of "four pounds per ton" is marked. A similar relationship for acid mist is presented in Figure 8 comparing "pound per ton" and "mg per scf". This basic format will be used to present much of the data from operating plants collected in the study.

The steady state data in Table 2 can be used for comparison to information obtained during plant malfunctions. A variety of malfunctions were observed and appropriate data concerning these malfunctions are presented in Section VI - "Analysis of Process Variables and Emissions". Malfunction data obtained included many start-up conditions for single absorption acid plants equipped with either ammonia scrubbers or sodium scrubbers, and for dual absorption acid plants. Data were obtained on a dual absorption acid plant (plant Q) showing the effect on SO_2 emissions of catalyst ageing, burning bright and dark sulfur, loss of absorber acid concentration, and loss of sulfur feedstock. Data from plant "J" shows the effect of inlet SO_2 variations on SO_2 emissions, and converter

TABLE 3

EPA NEW SOURCE PERFORMANCE STANDARDS TEST DATA

DUAL ABSORPTION CONTACT ACID PLANT
(PLANT "Q")

	Traverse scfm	H_2SO_4 (Acid Mist)		SO_2	
		lb/cf	lb/Ton Acid	lb/cf	lb/ton Acid
Sample #1	106,593	5.59×10^{-7}	0.055	1.66×10^{-5}	1.64
Sample #2	99,472	4.25×10^{-7}	0.037	1.61×10^{-5}	1.42
Sample #3	96,262	5.60×10^{-7}	0.046	2.48×10^{-5}	2.04

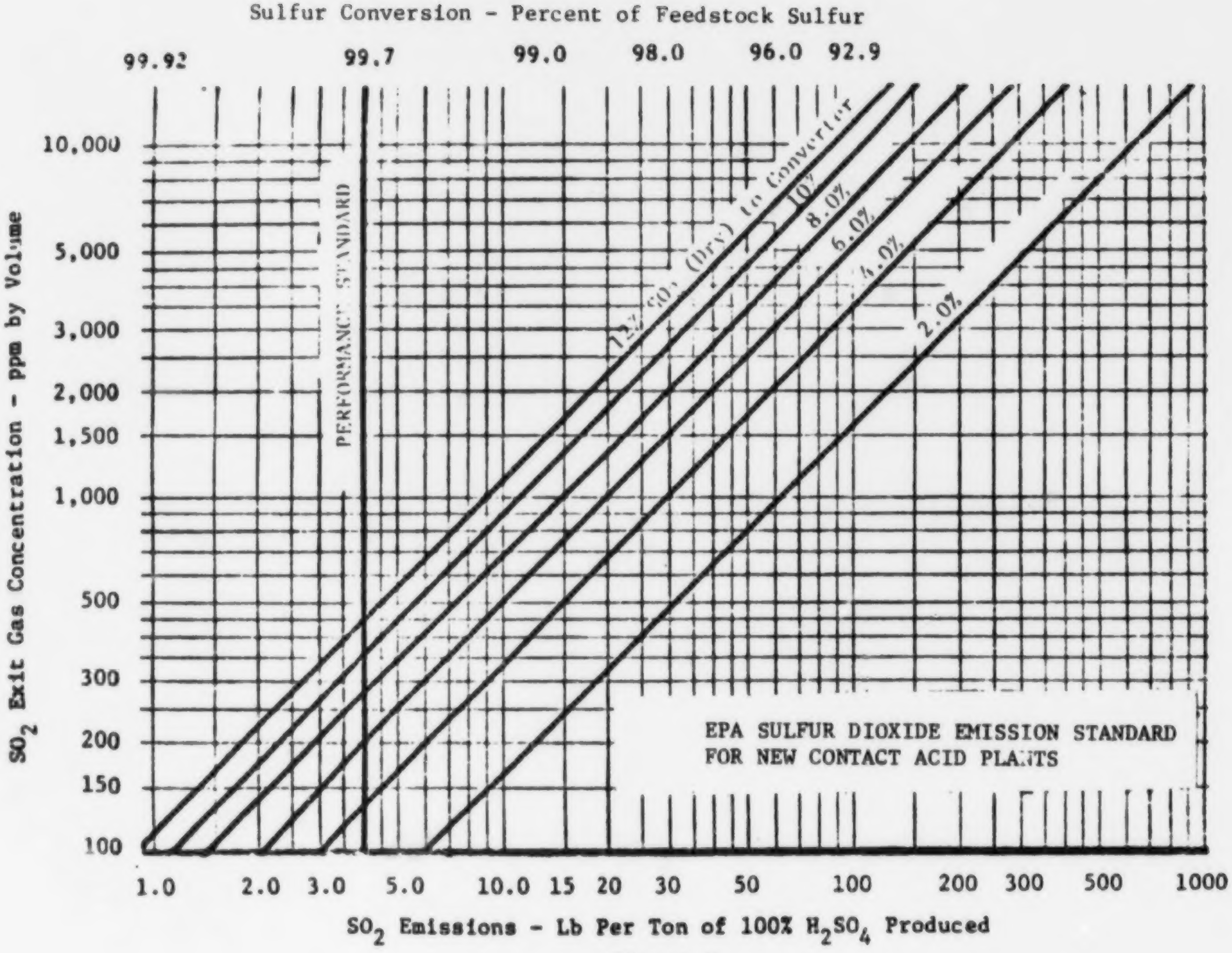

Sulfur Conversion - Percent of Feedstock Sulfur
99.92
99.7
99.0
98.0
96.0
92.9
10,000
5,000
3,000
2,000
1,500
1,000
500
300
200
150
100
SO_2 Exit Gas Concentration - ppm by Volume
1.0
2.0
3.0
5.0
10.0
15
20
30
50
100
200
300
500
1000
SO_2 Emissions - Lb Per Ton of 100% H_2SO_4 Produced
PERFORMANCE STANDARD
12% SO_2 (Dry) to Converter
10%
8.0%
6.0%
4.0%
2.0%
EPA SULFUR DIOXIDE EMISSION STANDARD
FOR NEW CONTACT ACID PLANTS

Figure 7

EPA ACID MIST EMISSIONSTANDARD FOR NEW CONTACT ACID PLANTS

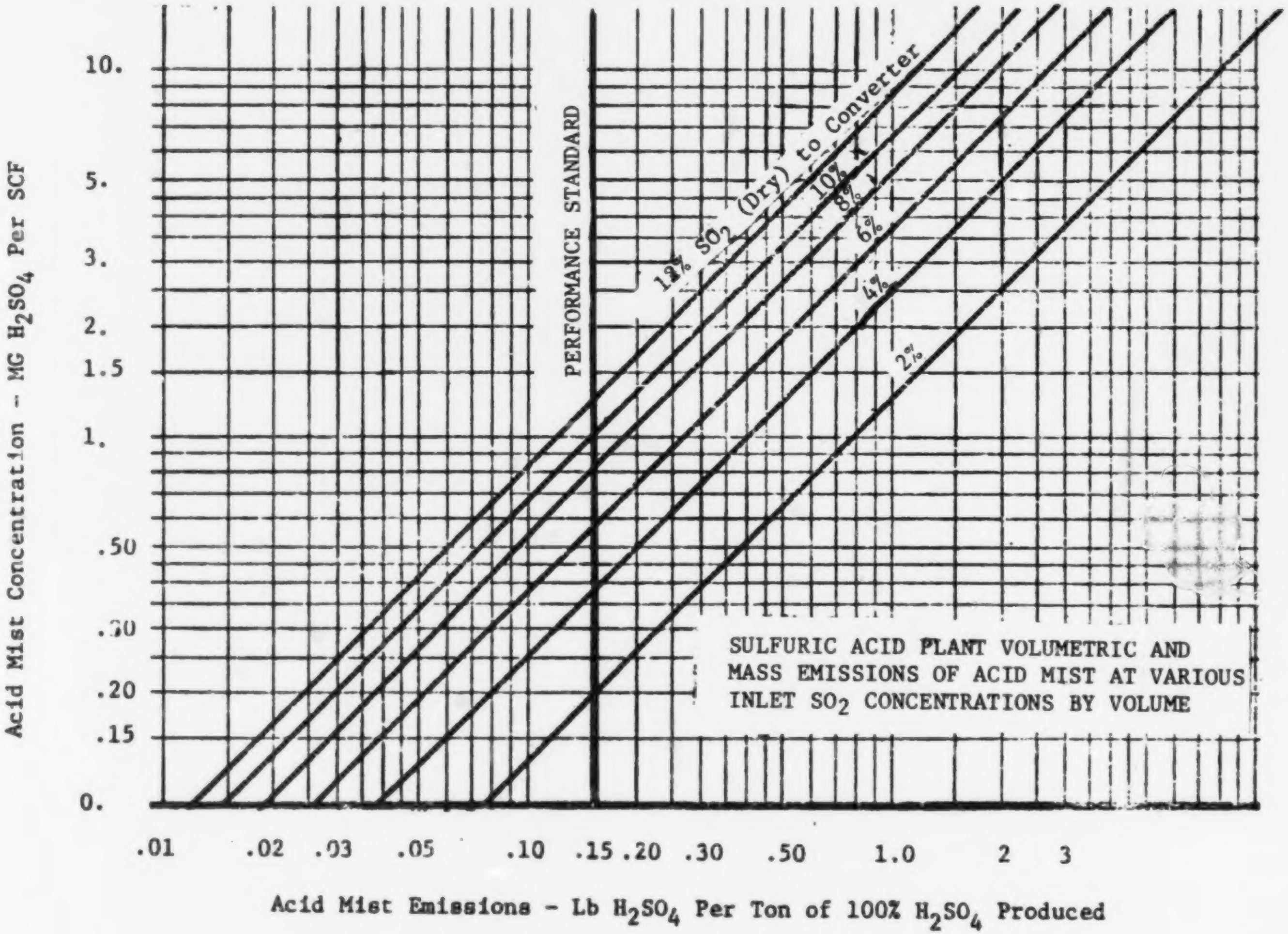


Figure 8

malfunctions, on a dual absorption plant. Data were obtained from a single absorption plant equipped with an ammonia scrubber (plants K and U) showing the effect on SO_2 emissions of pH control, specific gravity variations, effluent concentration variation from the ammonia scrubber, and deterioration of the scrubber packing. A single absorption acid plant with a sodium scrubber (plant Y) was studied during a loss of pH control in the sodium scrubber, specific gravity variations, and evaporator plugging in the reclaiming system. The effect of these malfunctions on SO_2 emissions is illustrated by the data.

An extensive study was made of the effect of downtime duration on SO_2 emissions during subsequent start-up. These data will be further analyzed in the next section to establish a criterion for converter reheat requirements with various shutdown periods.

SECTION VI

ANALYSIS OF PROCESS VARIABLES AND EMISSIONS

NORMAL PLANT OPERATIONS

The primary emphasis of this study is the relationship between process variables and emissions from contact sulfuric acid plants operating in upset conditions. The upset conditions have been classified as start-ups, shutdown, and malfunction or misoperation. In order to understand completely the nature of plant upset conditions and how the process variables effect emissions, it is necessary to review data obtained from plants in normal operation. The normal operating data were used to establish a basis for comparison with parameters during upset conditions.

Converter Temperature Control

The most important parameter for controlling sulfuric acid converter efficiency are temperatures in the catalyst bed. In normal operation the temperature of each bed is controlled by adjusting the heat transfer in the heat exchangers between converter stages. In normal operation a range of temperatures of one to three percent is permitted for the inlet temperature to each bed. Deviation from this range of temperatures will reduce the conversion efficiency of the catalyst. When temperatures are controlled within this range a specific converter efficiency is expected for each stage. The summation of the efficiencies of each stage represents the overall conversion for the plant. Typical converter temperature setpoints and

TABLE 4A

NORMAL STEADY STATE OPERATING TEMPERATURES AND CONVERSIONS IN EACH CONVERTER STAGE OF CONTACT ACID PLANTS

	Standard Single Absorption Operating Conditions (Plants U_1 and U_2)					Single Absorption With Air Quenching			EPA-NSPS Performance Test on Dual Absorption (Plant Q)							
	Temperature		Conversion	Range of Temp.					Temperature Ranges			Dual Absorption Test Runs(4)				
Location %, SO_2	°C	°F	%	°C	°F	°C	°F	% Conv.	°F Set Points	°F Temp. Range	% Conversion	1	2	3	4	5
Gas Entering First Pass	410.0	770		415-525	779-797	425	797		820°	770-830		795	797	800	803	806
Gas Leaving First Pass	601.8	1115		600	1112	612	1134			1100-1100		1098	1104	1118	1113	1118
Rise in Temp.	191.8	345	74.0	175-185	315-333	187	337	72.0		320-270	75	307	307	318	310	312
Gas Entering Second Pass	438.0	820		440-450	824-852	438	820		800°	800-830		828	830	843	845	845
Gas Leaving Second Pass	485.3	906		500	932	500	932			900-950		1001	1001	994	988	992
Rise In Temp. Cumulative Conversion	47.3	86	18.4 92.4%	50-60	90-108	62	112	21.0 93.0%		100-150	15 90%	173	179	151	143	147
Gas Entering Third Pass	432	810		435-440	815-824	439	822		800°	800-830		829	832	822	816	821
Gas Leaving Third Pass	443	830		450	842	448	838			830-860		884	886	865	859	363
Rise in Temp. Cumulative Conversion	11	20	4.3 96.7%	10-15	18-27	9	16	3.8 96.8%		30-60	6-7 96-97%	55	54	43	43	42
Gas Entering Fourth Pass	427.0	800		425-430	797-806	423	793		790°	800-830		832	834	820	815	821
Gas Leaving Fourth Pass	430.3	806		430-435	806-815	427	801			830-850		863	866	847	842	846
Rise in Temp. Cumulative Conversion	3.3	6	1.3 98.0%	5	9	4	8	7.7 99.5%		30-20	3.7-2.9 99.7-99.9%	31	32	27	27	25

*The high value is based on a Reich Test with an expected error of +1%, therefore the value for actual plant operation should be 98.5%.

ranges are given in Table 4A. This table also presents the expected conversion for each stage. Three major types of plants are included: single absorption, single absorption with air quenching, and dual absorption plants.

As shown in Table 4A an overall conversion efficiency of 98 percent is anticipated from a single absorption plant. The addition of air quench to a single absorption plant will increase the conversion efficiency to 99.5 percent. A dual absorption plant can obtain between 99.7 and 99.9 percent overall conversion efficiency. A series of five test runs on the dual absorption plant described in Table 4A shows the effect of catalyst bed inlet temperatures on the temperature rise across each bed and upon the conversion efficiency for each stage. This series of runs illustrates the need for close temperature control on catalyst bed inlet temperatures. The data presented in this table were obtained from previous EPA test.(4)

A study was made to determine a quantitative relationship between converter temperatures and SO_2 emissions in a dual absorption acid plant. A multiple linear regression analysis program was run using temperature and emission data from plant "J" during upset conditions to provide a wider range of temperature variations. An analysis was also performed on data taken from normal plant operations. The relationships developed in the analysis will be presented in a later section.

Several models were used in the regression analysis, with SO_2 as the dependent variable and converter temperatures as indepent variables. Complete computer results of this analysis is contained in Appendix C. The analysis of normal operating conditions was run on 30 data points selected at random from the plant "J" operating data. Six different regression models were used in an effort to establish correlation between SO_2 and temperatures. None of the correlations was significant. It is believed that the lack of significant correlation resulted from: (1) interdependency between temperatures, and (2) process parameters affecting SO_2 emissions that were not considered in the regression study. These variables include inlet SO_2 concentrations, sulfur furnace temperatures, and catalyst ageing. Because plant "J" is fed from a copper smelter and therefore has a highly variable imput concentration and flow rate, an additional regression analysis was performed on 31 random data points selected from normal operations from plant "Q". It was thought the more stable conditions of inlet concentration of SO_2 and other process variables might improve the correlation from the regression analysis. The correlations from this analysis were also included. After performing these two analysis it was concluded that a regression model of SO_2 emissions in terms of converter temperatures cannot be developed without additional data and study.

A base case was established for operation of double absorption acid plants by running standard statistical analysis on 64 random data points selected from normal operation of plant "J". This study was performed in an effort to confirm the information presented in Table 4A derived from a variety of sources of data. The results of the study on plant "J" indicates that if the eight converter temperatures are controlled within a specified range, the SO_2 emissions will be between zero and 307 ppm. The results of this study were highly significant and compared favorably to data presented in Table 4A. The results of this study are presented in Table 4B.

To further confirm the converter temperature ranges for normal SO_2 emissions 13 data points were selected from the data for plant "J" during times of high SO_2 emissions. Standard statistical analysis was performed on these data points and the mean temperatures calculated. Table 4C compares the mean temperatures from the normal run analysis and those from the off-normal analysis. The converter temperatures during upsets were consistently below the mean operating temperature for normal operations and generally fell outside of the acceptable range.

The statistical analysis comparing converter temperatures and SO_2 emissions confirms the data presented in Table 4A and clearly establishes the important relationships between these parameters. Some variation in acceptable temperature range will occur between plants because of variation in catalyst activity and types of catalysts. These data should be a good indication, however, of the acceptable ranges for modern dual

TABLE 4B

CONVERTER TEMPERATURE AND SO_2 OUTLET CONCENTRATION

PLANT "J" - UPSET CONDITIONS

Variable	Normal Run	Start-Up
	SO_2 Emissions (ppm)	
Y (ppm) SO_2 Exhaust Stack	127	1678
	Mean Temperature (°F)	
X_1 (°F) Inlet - 1st Converter Bed	824.0	815.0
X_2 (°F) Outlet - 1st Converter Bed	1040.9	1006.5
X_3 (°F) Inlet - 2nd Converter Bed	837.0	811.5
X_4 (°F) Outlet - 2nd Converter Bed	892.0	841.0
X_5 (°F) Inlet - 3rd Converter Bed	786.0	732.5
X_6 (°F) Outlet - 3rd Converter Bed	791.0	729.0
X_7 (°F) Inlet - 4th Converter Bed	762.0	702.0
X_8 (°F) Outlet - 4th Converter Bed	762.0	707.0

TABLE 4C

CONVERTER TEMPERATURES AND SO_2 OUTLET CONCENTRATION

PLANT "J" NORMAL OPERATION

Variable	Mean	Range
	SO_2 Emissions (ppm)	
(Y-1) ppm SO_2 Exhaust Stack	127	0-307
	Temperatures (°F)	
(X1) Temp (°F) Inlet - 1st Converter Bed	824	810-838
(X2) Temp (°F) Outlet - 1st Converter Bed	1041	948-1133
(X3) Temp (°F) Inlet - 2nd Converter Bed	837	891-855
(X4) Temp (°F) Outlet - 2nd Converter Bed	892	811-973
(X5) Temp (°F) Inlet - 3rd Converter Bed	786	734-838
(X6) Temp (°F) Outlet - 3rd Converter Bed	791	737-845
(X7) Temp (°F) Inlet - 4th Converter Bed	762	704-820
(X8) Temp (°F) Outlet - 4th Converter Bed	762	702-822

NORMAL RANGE OF OPERATION OF SINGLE ABSORPTION AND
DUAL ABSORPTION ACID PLANTS AS FOUND IN THIS STUDY

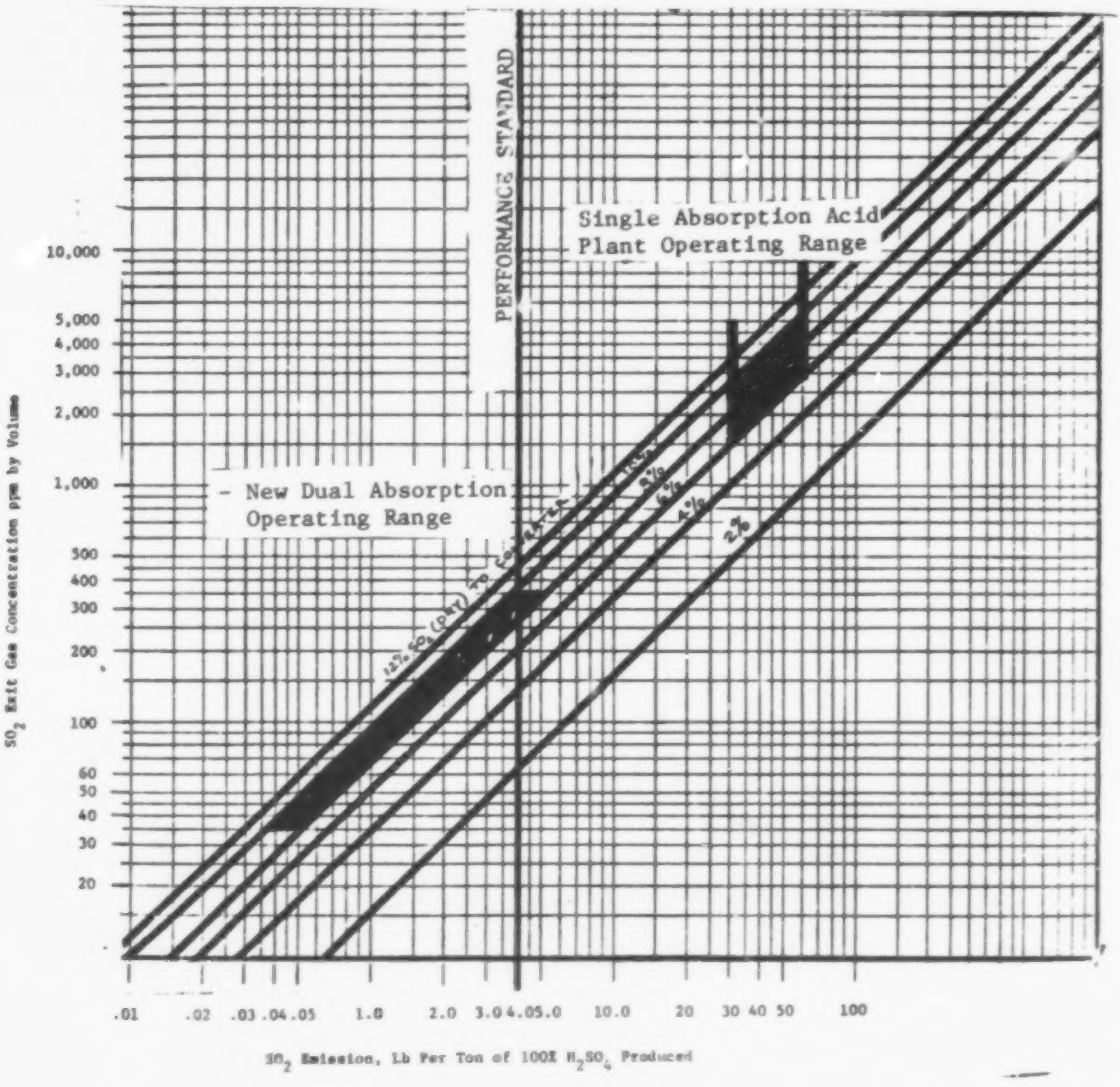


Figure 9

TABLE 5

PLANT "X" TEST DATA

Run. No.	Wt. % SO_2 Inlet (ppm)	Wt. % SO_2 Outlet (ppm)	Conversion Efficiency Percent	Tons Per Day Production	Average Opacity Percent
1	9.8	0.20	97.6	1025	0
2	9.8	0.20	97.6	1049	1.0
3	9.5	0.16	98.0	1049	9.5
4	9.2	0.20	97.6	1049	0.5
5	10.0	0.17	97.9	1049	5.0
6	9.8	0.18	97.8	1028	2.5
7	10.0	0.18	97.8	1028	2.5

absorption plants equipped with the newer types of catalyst.

Single Absorption Plants

The basic sulfuric acid producing plant for many years has been the single absorption type. This type plant has a long history of operation in contrast to the dual absorption plant and consequently a large amount of data are available. Even though the single absorption plant will not meet EPA standards (see Figure 9) it is important as a basis for studying the application of tailgas cleaning systems to single absorption plants and for supplementing data obtained from dual absorption plants.

Plant X shown in Table 2 of Section VI was selected as a typical single absorption plant to illustrate the SO_2 emissions and converter efficiency for this type of plant. The SO_2 conversion data, daily production rate, and opacity of the vent gas for plant X is shown in Table 5. This 1,000 ton per day acid plant was operating far in excess of allowable SO_2 emission standards and at times in violation of opacity standards.

The SO_2 emissions from plant X as shown in Table 5 fall within the range of SO_2 emissions for all single absorption plants studied. The SO_2 emissions ranged from 30 to 60 pounds per ton of 100 percent sulfuric acid produced.

Acid mist emissions originate from three separate sources. Because of the different form of the acid mist from these three sources, special provisions must be made for measuring the quantity of each type of mist emitted. Table 6 illustrates the amount of acid mist occurring in each of these types as measured by three separate analytical procedures. In the series of five tests shown, the EPA standard measurement method measures only the entrained acid carried over from the absorber. The results from this method are lower than those obtained using the special Monsanto method that measures, in addition to absorber carry-over the fine particulate acid mist formed in the absorber and SO_3 passing through the absorber. A comparison of the standard and special methods will show the standard method will always yield a result that is lower than the special method. In this particular single absorption acid plant located in the Northeastern United States, the acid mist standards were not violated, even when applying the special analysis method. These data were furnished from an EPA performance test.(5)

Though the single absorption acid plant shown in Table 6 could meet the acid mist standard, data from plant "U" covered in this study indicate that this plant cannot meet the acid mist standard. Data plotted in Figure 10 shows monthly averages of acid mist emissions over a period of six years. None of the points plotted fall within the performance standard. This data illustrates the need for special equipment to control acid mist emissions regardless of the type of plant considered.

As a contrast to data shown in Figure 9, Table 7 shows a sum-

TABLE 6

ACID MIST TEST
(DATA FURNISHED BY EPA)(5)

Test	Stack Gas Flow Rate scfm	lb H_2SO_4 per scf x 10^{-7}	mg H_2SO_4 per scf	Production Tons/Day (H_2SO_4)	Emission lbs H_2SO_4/Day	Emission lbs H_2SO_4/ Ton of Acid	
						Standard Method	Special Method
1A	20,737	5.37	0.224	185	16.04	0.087	
1B		2.29	0.096		6.84		
1C					22.88		0.12
2A	20,354	4.60	0.208	175	13.48	0.077	
2B		0.90	0.041		2.64		
2C		1.18	0.053		3.46		
					19.58		0.11
3A	20,958	4.40	0.200	175	13.28	0.076	
3B		0.78	0.036		2.35		
3C		0.94	0.043		2.84		
					18.47		0.11
4A	20,506	4.45	0.202	193	13.14	0.068	
4B		0.82	0.037		2.42		
4C		0.97	0.044		2.86		
					18.42		0.10
5A	20,549	4.57	0.207	193	13.52	0.070	
5B		0.94	0.043		2.78		
5C		0.90	0.041		2.66		
					18.96		0.10

Monthly Variations in Acid Mist Emission Over the Past Six Years
(Plant U_1, Bright Sulfur Burned in a Single Absorption Contact Acid Plant)

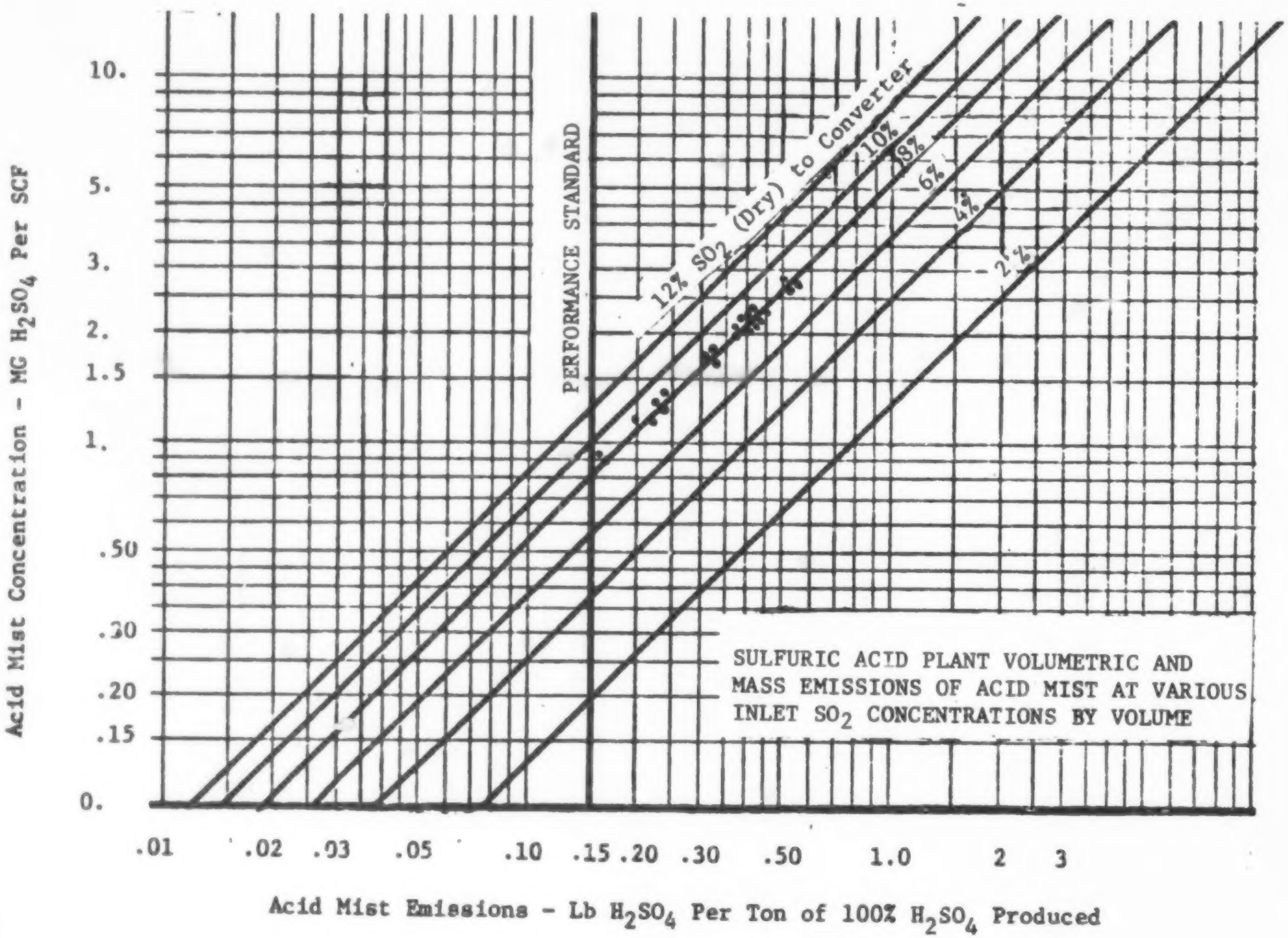


Figure 10

TABLE 7

ACID MIST OBSERVATIONS (6)
(DATA FURNISHED BY EPA)

Location	Company	Feedstock	Process	Mist Eliminator	Acid Mist, Lbs/Ton	Opacity, %	Temp. °F	Relative Humidity, %	Sky Cover	Comments
Paulsboro, N. J.	Olin Corp.	Spent Acid, S	Single Abs. + Wellman - PG	Brink H. E.	—	0	25	55	9/10	Water Plume
Linden, N. J.	American Cyanamid Corporation	Dark S	Dual Abs.	Brink H. E. followed by Brink H. V.	—	0	31	61	10/10	
					0.02	0	39	51	10/10	
					0.08, 0.02	0	50	57	4/10	Late PM Light Snow
Paulsboro, N. J.	Olin Corp.	Spent Acid, S	Single Abs. + Wellman - PG Na$_2$SO$_3$ Scrubber	Brink H. E.	—	0	51	48	9/10	Water Plume
					—	0	46	46	5/10	Down @ 8:30 a.m.
					—	0	—	—	--	Water Plume
					—	0	36	42	10/10	Water Plume
					0.04, 0.15	0	47	24	0	Water Plume
					—	0	59	22	0	Water Plume
					—	0	65	54	10/10	Water Plume
					—	0	85	46	2/10	No Water Plume
Elizabeth, N. J.	Allied Chemical Corporation	Spent Acid, S	Single Absorption	Brink H. E.	—	0	84	55	10/10	Clear Blue sky in a.m.
					0.09	0	76	45	10/10	
					0.08, 0.08	0	78	36	8/10	
					—	0	76	54	10/10	
Newark, N. J.	Essex Chemical	Dark S	Single Abs.	Brink H. E.	—	<10	84	55	10/10	
Linden, N. J.	DuPont, Grasselli Works	Bright S	Single Abs.	Pebble Bed	—	40	84	55	10/10	
Gibbstown, N. J.	DuPont, Repauno Works	Dark S	Single Abs.	Intalox Saddles	—	30	85	46	2/10	
Deepwater, N. J.	DuPont, Chambers Works	Dark S	Single Abs.	Intalox Saddles	—	0	85	46	2/10	
Newell, Pa.	Allied Chemical Corporation	Pyrites, S Spent Acid	Single Abs.	NH$_3$ Scrubber followed by Brink H. E.	--	10 to 20	74	51	9/10	Brink elements may be leaking. No water plume.

mary of acid plants tested by EPA that will generally meet the acid mist performance standards. All these plants were burning spent acid or dark sulfur, contributing to an increased acid mist evolution. A review of the acid mist emissions and opacity for these plants shows that the application of a packed fiber filter (Brink) will eliminate all acid mist carry-over contributing to opacity. In two cases, plants equipped with filters packed with pebbles or Intalox saddles had a vent gas stream with opacity of 30 to 40 percent. This type of packed bed has a low removal efficiency for the very small particle size of the acid mist. The Newell, Pennsylvania plant was equipped with a Brink filter and had an opacity reading of 10 to 20 percent. The high opacity reading in the vent gas probably indicated the Brink filter was leaking. An important conclusion that can be drawn from the data of Table 7 is that a single absorption acid plant equipped with a vent gas cleaning system must also be equipped with an efficient filter for eliminating acid mist and high opacity in the vent gas.

Single Absorption Plants with Gas Cleaning Systems

The need for acid mist filters on a single absorption plant equipped with a vent gas cleaning system was indicated in the previous paragraph and in Table 7. It has also been previously indicated that the single absorption plant cannot reach the SO_2 emissions standards without provisions for removing SO_2 from the vent gas.

When a single absorption plant, however, is equipped with proper acid mist filters and an efficient vent gas cleaning system, both the SO_2 and acid mist performance standards can be met. Data obtained in our study from plant "Y" is shown in Table 8. Plant "Y" is a single absorption acid plant equipped with a sodium scrubber system and acid mist entrainment filters. As indicated in Table 8 this plant in normal operation can reach an SO_2 emission level of 2.59 pounds per ton and an acid mist emission level of .043 pounds per ton. In a series of three tests, Test 1 was discarded because of possible sampling equipment failure. Test 3 was run at a higher gas flow rate than Test 2 and produced acid mist emissions equal to the performance standard of .05 pounds per ton. Although the tendency toward increased acid mist emissions at higher gas rates is expected, the cause and effect relationship of this data cannot be substantiated.

Dual Absorption Plants

The primary difference between the single absorption acid plant and the dual absorption plant is the installation of a primary absorber following the third catalyst bed. A primary absorber in this location reduces the SO_3 concentration of the gas entering the fourth catalyst stage. Removing SO_3 from this gas permits a higher driving force in the fourth converter stage to shift the conversion equilibrium in the direction of more SO_3 formation. The effect of the primary absorber on overall conversion efficiency is illustrated in Table 9.

TABLE 8

EPA PERFORMANCE TEST RESULTS FOR SO_2 AND ACID MIST EMISSION CONTROL EFFECTIVENESS FROM SODIUM SCRUBBER

(PLANT "Y")

Test No.	Gas Flow (SCFM)	Production Rate (Tons/Day)	SO_2 (Outlet)			SO_3 + Acid Mist (Outlet)	
			PPM	Lb/Ton	H_2SO_4 (ppm)	H_2SO_4 (lb/SCF)	H_2SO_4 (Lb/Ton)
2	35,141	730	250	2.59	2.26	0.279	0.043
3	36,292	730	227	2.85	7.79	0.965	0.162

TABLE 9

EFFECT OF PRIMARY ABSORBER IN THE DUAL ABSORPTION PROCESS

(PLANT "Q")

(Basis 100 mols Feed Gas at 9.0% SO_2 and 12% O_2)

Converter Feed Gas Vol. % SO_2	9.00	12.00	0	79.0	100.00	
97% Conversion	-8.73	-4.365	+8.73	0	-4.365	
To First Absorber Vol. % SO_2	0.27	7.635	8.73	79.0	95.635	2700
SO_3 Absorbed	0	0	-8.73	0	-8.730	
to Fourth Catalyst Vol. % SO_2	0.270	7.635	0	79.0	86.905	2700
97% Conversion	-0.262	-0.131	+0.262	0	-0.131	
To Final Absorber Vol. % SO_2	0.008	7.504	0.262	79.0	86.774	81
SO_3 Absorbed	0	0	-0.262	0	-0.262	
To Exit Stack	0.008	7.504	0	79.0	86.512	81
Volume, % SO_2	.0081					
Volume, ppm SO_2	81					

Overall Conversion Efficiency 99.91%

As indicated in Table 9, the SO_2 to SO_3 conversion in the first three sections of the catalyst converter reaches a total of 97 percent. If this gas were sent directly to the fourth catalyst bed an additional conversion of 1.3 percent could be expected as indicated in the review of the single absorption plant presented in Table 4A of Section VI. This will give an overall conversion efficiency for a single absorption plant of 98.3 percent.

The addition of the primary absorber after the third catalyst stage, however, will reduce the SO_3 concentration in the gas entering the fourth catalyst bed to essentially zero. The remaining SO_2 can now be converted in the fourth catalyst stage to an additional extent of 3.8 percent (based on original SO_2 present) providing an overall conversion efficiency 99.91 percent. This high overall conversion efficiency reduces the SO_2 concentration in the vent gas to less than 100 ppm.

The result of this increased SO_2 conversion efficiency can be seen in test data obtained from plant "Q". These data presented in Table 10 show results of three performance test runs measuring SO_2 and acid mist emissions. During these tests the plant was operating somewhat higher than design capacity, as indicated by the emission results based upon actual production rates and design production rates. Comparison to the performance standards indicates the plant was operating well below the standards at all times.

TABLE 10

SUMMARY OF TEST RESULTS FROM DUAL ABSORPTION

PLANT "Q"

SO_2 Emissions, lb/ton	Test No. 1	Test No. 2	Test No. 3	NSPS
Based on actual production	1.66	1.43	2.06	4.0
Based on design rate	1.69	1.52	2.28	4.0
Based on actual production adjusted for higher in-stack monitor readings	2.17	1.86	2.85	4.0
Acid Mist Emissions, lb/ton				
Based on actual production	0.056	0.037	0.046	0.15
Based on design rate	0.057	0.039	0.051	0.15

Plant "Q" was typical of all dual absorption plants in normal operation. The range of SO_2 emissions from all plants studied was presented in Figure 9 (Page 57) in the preceding section on single absorption plants. This figure also shows the range of emissions from dual absorption plants. Plant "Q" falls approximately mid-way in this range. This figure also illustrates that essentially all the data obtained from dual absorption plants for SO_2 emissions fall below the performance standard limit.

Figure 11 further illustrates the SO_2 emissions from single and double absorption plants operating under normal conditions. In addition to showing the minimum, maximum, and average emissions for the single absorption and double absorption plants, Figure 11 also indicates the range of emissions experienced during initial operation of new plants. During the initial operation of a new plant in good operating order, the SO_2 emissions will fall between 1.5 and two pounds per ton of 100 percent sulfuric acid produced.

Another important fact illustrated by Figure 11 is the effect of higher concentration of SO_2 entering the converter of the double absorption plant (eight to ten percent). For a single absorption plant the maximum SO_2 concentration in the feed gas to the converter was eight percent. High SO_2 feed concentrations and higher conversion efficiencies both promote increased production from the dual absorption acid plant and more efficient and economical overall operation.

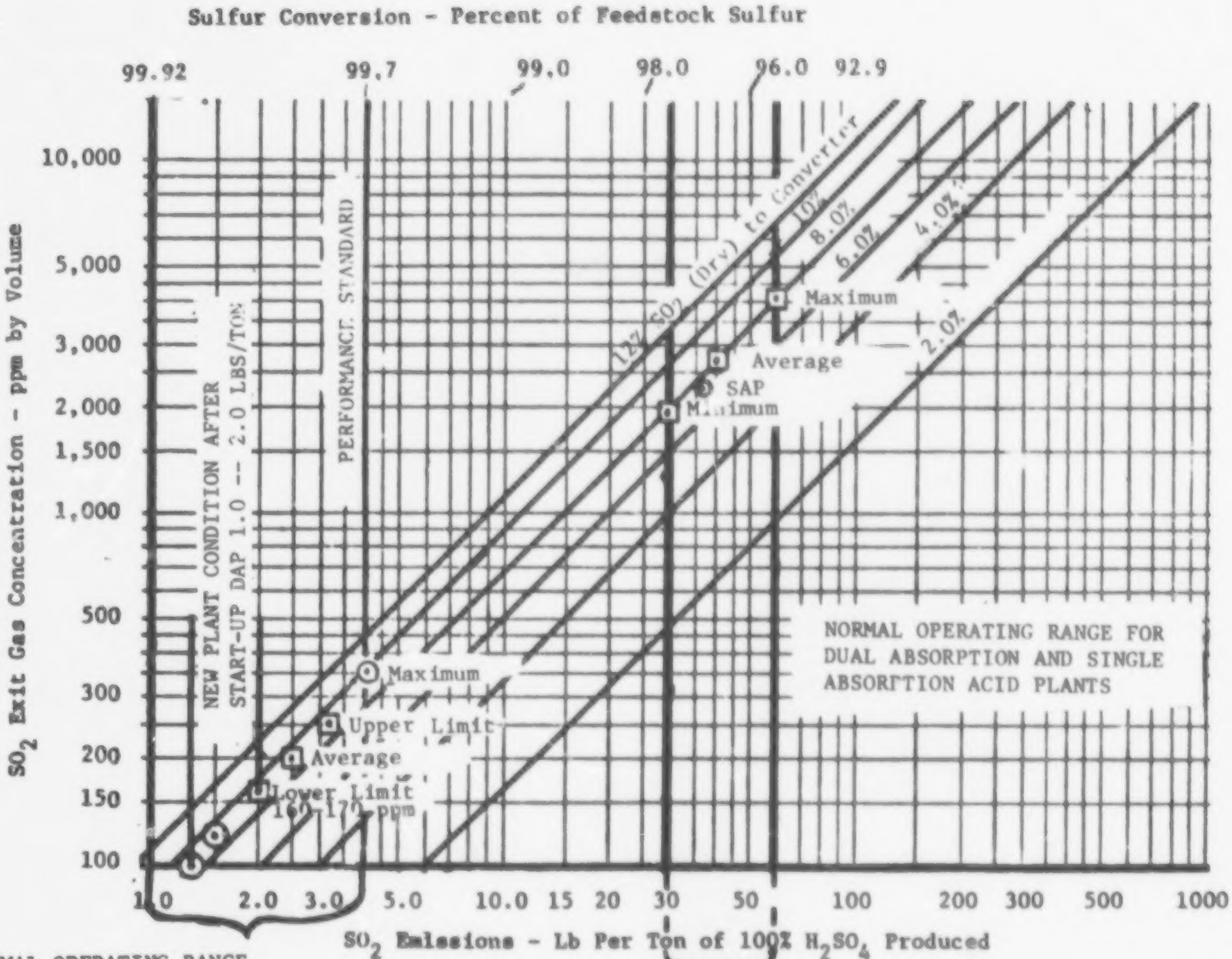

Sulfur Conversion - Percent of Feedstock Sulfur
99.92
99.7
99.0
98.0
96.0
92.9
10,000
5,000
3,000
2,000
1,500
1,000
500
300
200
150
100
SO_2 Exit Gas Concentration - ppm by Volume
1.0
2.0
3.0
5.0
10.0
15
20
30
50
100
200
300
500
1000
SO_2 Emissions - Lb Per Ton of 100% H_2SO_4 Produced
12% SO_2 (Dry) to Converter
10%
8.0%
6.0%
4.0%
2.0%
NEW PLANT CONDITION AFTER
START-UP DAP 1.0 -- 2.0 LBS/TON
PERFORMANCE STANDARD
Maximum
Upper Limit
Average
Lower Limit
160-170 ppm
Maximum
Average
SAP
Minimum
NORMAL OPERATING RANGE FOR
DUAL ABSORPTION AND SINGLE
ABSORPTION ACID PLANTS
THE NORMAL OPERATING RANGE
FOR DUAL ABSORPTION PLANT
THE NORMAL OPERATING RANGE
FOR SINGLE ABSORPTION PLANT

Figure 11

SHUTDOWN OPERATION

The operation of shutting down a contact sulfuric acid plant does not necessarily produce SO_2 or acid mist emissions in excess of performance standards. If the proper shutdown procedure is followed, most emissions associated with the shutdown originate from a malfunction or upset that is also the cause of shutdown. The most important aspect of the shutdown procedure is preparation of the plant for subsequent start-up to minimize start-up emissions. In this section we discuss shutdown operations as they affect emissions on the start-up of a dual absorption acid plant. Our primary attention is applied to the length of the shutdown period compared to emissions on restarting the plant.

The data obtained from most of the plants studied did not contain a sufficient number of shutdown operations to provide a basis for statistical analysis of shutdown duration compared to start-up emissions. Data from plant "J", however, was collected over a long period of time, including many shutdown and start-up operations. The monitoring program for plant "J" from which the data was extracted covered a period of 5,088 hours or 212 days.(7) During this period of time the acid plant was in operation for a total of 190 days or 90 percent of the time period. After accounting for periods of inoperation of the plant and emission monitoring instrumentation, data were collected during 86 percent of the period of the monitoring program. The monitoring instrumentation recorded one reading for each process parameter every three minutes. At the end of each 15 minute interval the average of the previous five readings was computed. These fifteen minute averages were used as the basic data points for analyzing the performance of the plant. During this period of operation, data for 23 start-ups were obtained after plant shutdowns ranging from 30 minutes to five days.

To simplify the analysis for the plant shutdowns, shutdown periods were divided according to duration of the shutdown in categories of less than one hour, one to two hours, two to six hours, six to ten hour, 10 to 15 hours and over 15 hours. The sulfur dioxide emissions from the plant during start-up, from the beginning of the start-up operation through the sixth hour after start-up operations began, were plotted against time using a linear regression analysis program on a computer. The sulfur dioxide emissions were used as the dependent variable and operation time as the independent variable. Regression curves were plotted by the computer averaging all the data points in each category on each hour of operation during the start-up period. A summary of these regression plots is presented in Table 11.

A review of Table 11 shows that data from two to six start-up operations were included in each of the six categories. In the "less than one hour", category where only two start-ups were observed, the confidence level of the results is quite low. For those categories containing larger numbers of

TABLE 11

THE EFFECT OF DOWNTIME SHUTDOWN DURATIONS UPON

EFFLUENT SO_2 CONCENTRATIONS (VOL. ppm) DURING START-UP
(FOR PLANT "J")

Shutdown Duration Hours	Peak SO_2; ppm During Startup	Hours to reach 300 ppm SO_2	Number of Startup Cases	Reading at 4th Hour (SO_2-ppm)
<1	185	--	2	64
1 - 2	520	--	5	123
2 - 6	1,920	4.4	3	350
6 - 10	1,600	3.50	3	275
10 - 15	2,250	4.80	4	400
15+	2,970	5.70	6	749

start-ups a greater confidence level can be assigned. Considered as a total analysis the results have high significance. Comparison of the "hours to reach 300 ppm" for each category indicates the operation time to compliance with the standards increases with increased duration of shutdown. This time curve flattens, however, at approximately six hours, indicating that with normal start-up operations all plants should be able to come within compliance within six hours. It is also apparent that the longer the shutdown period, the higher the peak SO_2 emissions during the start-up operation. This analysis shows that most of the start-up operations approached 300 ppm at the fourth hour, indicating that most plants can be started up within four hours with SO_2 concentration reduced to the performance standards regardless of the length of the shutdown duration.

The start-up analysis provided here must be evaluated in terms of the type of plant providing the operational data. Plant "J" is a sulfuric acid plant using the dual absorption design with SO_2 feed from a copper smelter. Because of the nature of the SO_2 feed, concentration of SO_2 entering the converter varies from 1.6 to 19 percent. Also, the start-up of the acid plant is dependent upon start-up problems within the smelter, giving a much wider variation in start-up conditions than would be expected from the same type of plant operating with elemental sulfur feed. The peak SO_2 concentration reached during start-up is probably the parameter most affected by the variation in start-up conditions of the smelter.

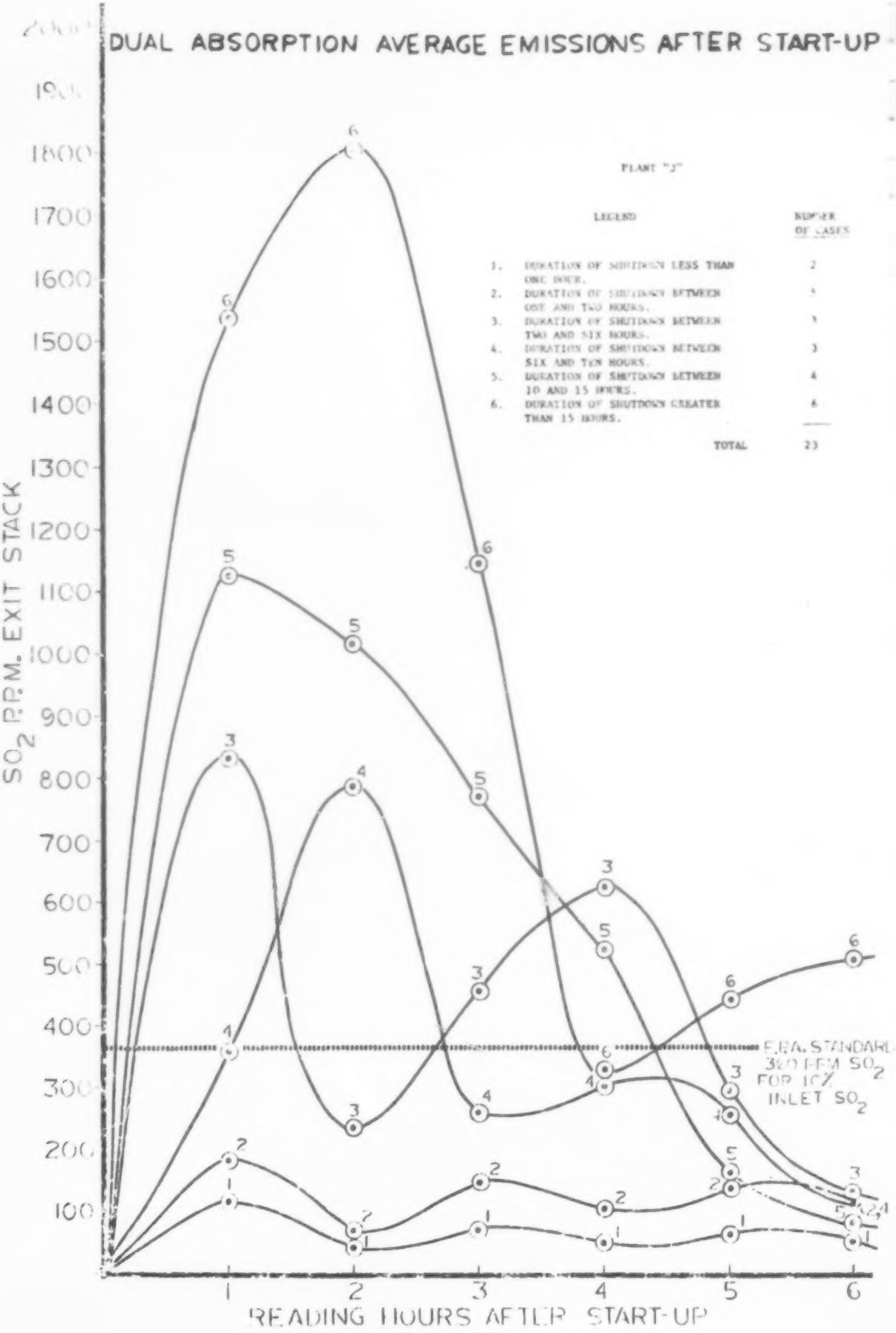

DUAL ABSORPTION AVERAGE EMISSIONS AFTER START-UP
PLANT "J"
LEGEND
NUMBER OF CASES
1. DURATION OF SHUTDOWN LESS THAN ONE HOUR. 2
2. DURATION OF SHUTDOWN BETWEEN ONE AND TWO HOURS. 5
3. DURATION OF SHUTDOWN BETWEEN TWO AND SIX HOURS. 3
4. DURATION OF SHUTDOWN BETWEEN SIX AND TEN HOURS. 3
5. DURATION OF SHUTDOWN BETWEEN 10 AND 15 HOURS. 4
6. DURATION OF SHUTDOWN GREATER THAN 15 HOURS. 6
TOTAL 23
E.P.A. STANDARD 350 PPM SO2 FOR 10% INLET SO2
SO2 PPM. EXIT STACK
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
1
2
3
4
5
6
READING HOURS AFTER START-UP

Figure 12

TABLE 12

SUMMARY OF START-UP OPERATIONAL DATA ON DUAL (DAP) AND SINGLE (SAP) ABSORPTION ACID PLANTS FOR FIGURES 25 THROUGH 41

Fig. No.	Type of Plant	Downtime Duration (Hours)	Time Required To Reach Normal Operating Level (Hours)	Time SO_2 Emissions Exceeded EPA Standard of 300 ppm (Hours)	Peak SO_2 Emissions (Vol. ppm)	Comments
25	DAP	12.5	6.5	3.0	1800	
26	DAP	51.5	2.5	2.0	1500	
27	DAP	6.5	5.5	4.5	1600	
28	DAP	6.0	7.0	5.0	1200	
29	DAP	16.5	5.0	4.0	1500	
30	DAP	9.0	6.0	2.0	700	
31	DAP	5.5	3.0	2.0	2000	
32	SAP	12.0	--	--	4000	Scrubber Down for 28 hours - Plant not in Compliance at Anytime
33	DAP	37.0	7.0	5.5	2900	
34	DAP	16.0	15.0	11.0	2800	
35	DAP	13.5	3.5	2.5	2400	
36	DAP	16.5	7.0	6.5	3100	
37	DAP	10.5	6.0	4.5	3100	
38	DAP	9.0	5.0	3.0	1500	
39	DAP	Incomplete	2.0	Incomplete	950	
40	DAP	Data		Data		
41	DAP	1.0	1.5	1.5	2200	
		160.0	5.2	4.0	3000	

To provide a more realistic presentation of the start-up data for the 23 cases presented in Table 11, arithmetic averages of SO_2 concentration for each hour of start-up within each category of downtime were plotted on Figure 12. The use of arithmetic averages and time plots show the cyclic nature of most plant start-up operations and the increase in maximum SO_2 concentration with increased shutdown duration period. This plot also shows that most shutdown and start-up cycles will provide SO_2 emissions below EPA standards within six hours. With the exception of very long shutdowns, exceeding ten hours, the plant can be brought to compliance within about four hours. The four hour shutdown-period-breakpoint for heat conservation and restart without reheating the plant is also illustrated by this curve. The EPA standard of 360 ppm for a 10 percent inlet SO_2 concentration is shown. This is typical for dual absorption acid plants but may be high for a plant fed from a copper smelter.

Concentrations of SO_2 during start-up were obtained for most of the dual absorption plants studied, providing data from a variety of plants in a variety of shutdown and start-up conditions. SO_2 concentration was plotted against time at the beginning of the start-up operation for each of these data sets. This information is presented of Figures 25 through 41 included in Appendix B. These figures are summarized in Table 12. The data, taken from plants burning elemental sulfur and using the dual absorption process, generally confirm the information obtained from the regression analysis on plant "J".

A general summation of all of the plant start-up data indicates most plants can reach compliance within four hours regardless of the shutdown period, and essentially all plants can be below 300 ppm after six hours of start-up operations. Also verified is the four-hour maximum shutdown duration before reheat of the converter is required to insure SO_2 emissions of less than 300 ppm during the start-up operations. These data and conclusions apply to typical sulfuric acid plants in normal operation with no special precautions for minimizing SO_2 emissions (such as maintaining low production rates during initial operation periods or using heat and hot concentrated acid from associated plants to assist in the start-up operation). This data also include the occurrence of normal upsets and equipment failures during the start-up operation resulting in higher SO_2 emissions during some operations.

START-UP OPERATIONS

Single Absorption Plants

During the course of this study data were not collected on single absorption contact acid plants unless they were equipped with a vent gas cleaning system permitting them to meet emissions standards. Understanding of the start-up procedure on a single absorption plant, however, is important to the evaluation of the operation of the vent gas cleaning systems. Start-up data from two identical single absorption acid plants (Plants U_1 and U_2) is shown in Tables 13 and 14, and 15 and 16 respectively in the next section (page 81).

A review of converter temperatures tabulated for these plants indicates that all temperatures were controlled acceptably during the entire start-up operations. One variation in temperatures, however, occurred that might be considered a cause of high SO_2 emissions. As shown in Tables 15 and 16, the peak emissions of SO_2 from plant U_2 occurred at a point where the inlet temperature of the catalyst mass B was also at a peak. The outlet temperature for mass B in the preceding reading was also high indicating this temperature was somewhat out of control. Since insufficient data were available from these plants to run a statistical analysis, conclusive relationships between catalyst bed temperatures and SO_2 emissions cannot be established. A general evaluation of this plant operation, however, indicates that the peak SO_2 occurred approximately two hours after start-up, which is normal for a single absorption plant of this type.

A review of furnace temperatures for plant U_1 presented in Table 13 indicates full sulfur feed to the furnace was not established until approximately five hours into the start-up operation. A reduction of SO_2 entering the converter contributed to the relatively low concentration of SO_2 emissions from this plant during this start-up. If full sulfur feed had been applied to the furnace at the beginning of the start-up operation, SO_2 concentration exit the absorber tower would have reached approximately 4,000 ppm rather than the 3,000 ppm experienced.

TABLE 13

START-UP TEMPERATURES FOR PLANT "U_1"
SINGLE ABSORPTION ACID PLANT WITH AMMONIA SCRUBBER

Time	Furnace Temp °F	Boiler Exit	A - Mass Entrance	A - Mass Exit	B - Mass Entrance	B - Mass Exit	C - Mass Entrance	C - Mass Exit	D - Mass Entrance	D - Mass Exit	98% Acid Inlet Temp.	Acid Temperature Exit Absorption Tower
2:45	1710	602	836	1093	815	869	826	862	804	716	174	
3:00	1710	602	834	1092	819	899	832	865	823	740	175	
3:15	1712	605	834	1091	820	911	836	870	811	803	176	200
3:30	1704	606	832	1092	821	920	834	874	802	825	180	203
3:45	1710	607	834	1092	823	926	828	877	829	817	183	201
4:00	1710	607	830	1091	825	931	828	873	841	830	185	206
4:15	1728	609	829	1090	824	931	827	871	818	841	187	210
4:30	1732	610	832	1092	826	932	829	870	801	846	187	212
4:45	1738	610	832	1093	826	934	830	874	798	829	189	213
8:00	1748	611	831	1095	826	936	833	877	797	812	190	213
5:15	1744	614	832	1096	827	936	834	879	799	811	190	215
5:30	1738	612	828	1094	828	937	835	879	800	811	191	217
5:45	1731	609	824	1090	826	939	834	879	800	813	192	216
6:00	1721	607	824	1089	826	939	834	879	800	813	192	216
6:15	1728	607	820	1086	827	939	834	879	800	813	192	216
6:30	1728	610	820	1084	827	939	834	879	800	813	193	218
6:45		610	824	1082	831	939	834	879	800	813	194	219
7:00			822	1083	829	939	834	879	800	813	195	218
7:30	1750	610	822	1081	826	936	834	877	800	812	198	219
7:45	1800	625	830	1091	826	939	835	882	800	812	204	227
8:00												
8:15	1805	627	841	1094	839	945	840	892	810	807	206	229
8:30	1807	629	836	1100	839	949	840	895	840	821	208	229
8:45	1806	629	831	1100	832	949	845	896	812	824	208	233
9:15	1900	630	829	1096	837	952	849	901	816	829	204	232

NOTE: All Temperatures are in °F.

TABLE 14

START-UP PLANT "U_1"

AMMONIA SCRUBBER CONDITIONS AND EMISSIONS DURING ACID PLANT START-UP

Time	% SO_2 Entrance to Converter	% SO_2 Absorbing Tower Exit
2:30 PM	---	.24
2:45	---	.22
3:00	---	.208
3:15	7.6	.30
3:45	7.9	.335
4:00	8.8	.23
4:15		.245
4:45	9.2	.235
5:00	8.6	.205
5:15		.20
5:30	8.4	.195
5:45		.205
6:00	8.4	.19

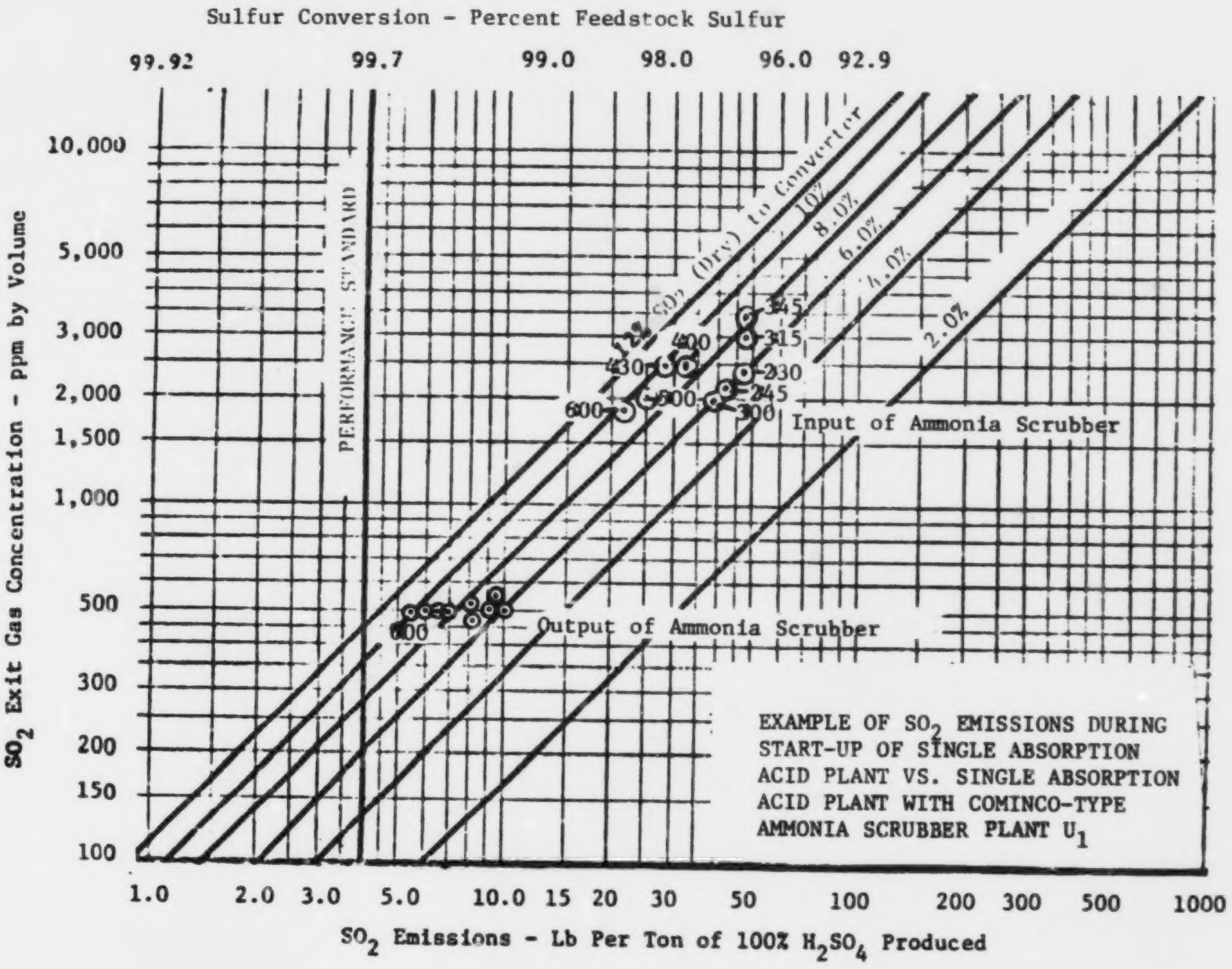
Sulfur Conversion - Percent Feedstock Sulfur
99.92
99.7
99.0
98.0
96.0
92.9
SO2 Exit Gas Concentration - ppm by Volume
10,000
5,000
3,000
2,000
1,500
1,000
500
300
200
150
100
PERFORMANCE STANDARD
SO2 (Dry) to Converter
12%
10%
8.0%
6.0%
4.0%
2.0%
345
315
230
245
300
400
430
500
600
Input of Ammonia Scrubber
Output of Ammonia Scrubber
EXAMPLE OF SO2 EMISSIONS DURING
START-UP OF SINGLE ABSORPTION
ACID PLANT VS. SINGLE ABSORPTION
ACID PLANT WITH COMINCO-TYPE
AMMONIA SCRUBBER PLANT U1
1.0
2.0
3.0
5.0
10.0
15
20
30
50
100
200
300
500
1000
SO2 Emissions - Lb Per Ton of 100% H2SO4 Produced

Figure 13

The only operating parameter for plant U_1 that seems to be abnormal is the temperature of the acid in the absorber. This temperature is somewhat higher than normal, possibly indicating a shortage of cooling water for the acid coolers in the absorption system. This high temperature possibly contributed to an increase in acid mist emissions although confirmation of this fact is not available in the data.

Single Absorption Plant with Vent Gas Cleaning Systems

Plants U_1 and U_2 described in the previous section are equipped with ammonia scrubber vent gas cleaning systems. Extensive data were obtained from these two plants in various modes of operation. The temperature profile across plant U_1 is presented in Table 13, while absorber operating conditions are presented in Table 14. The performance of the ammonia scrubber applied to plant U_1 is illustrated in Figure 13.

A significant feature of Figure 13 is the illustration of constant SO_2 concentration from the ammonia scrubber in terms of parts per million by volume over a range of scrubber inlet SO_2 concentration of 1,900 ppm to 3,350 ppm. This comparison illustrates the lack of precision in defining SO_2 emissions on the basis of ppm in the vent gas. When calculated in terms of pounds of SO_2 per ton of acid produced the output from the ammonia scrubber varied from 5.5 to 10 pounds per ton. SO_2 emissions presented in mass units much more clearly illustrate the effect of variable input concentrations of SO_2 to the ammonia scrubber. Although plant U_2 showed a performance of

5.5 to 10 pounds of SO_2 per ton of acid produced, this plant is capable of producing vent gas containing less than four pounds per ton during periods of careful operation and no malfunction.

Start-up data for plant U_2 is presented in Table 15 and 16, with ammonia scrubber performance in Figure 14. Plant U_2 is identical to plant U_1, and comparison of temperature profile across the plant and the SO_2 concentration differential across the converter indicates the two acid plants were operating in very similar manner. Comparison of the SO_2 emissions from the ammonia scrubber, however, indicates a great difference in operation between the scrubbers on plants U_1 and plant U_2. During the start-up operation of plant U_2, the vent gas booster blower used in conjunction with the Brink filter in the scrubber outlet was not in operation. This blower was shutdown because of lack of steam for driving the turbine. With the blower shutdown and the Brink filter bypassed, a very dense plume of particulate matter was being emitted from the ammonia scrubber. Since all process parameters for the two scrubber systems are similar except for the SO_2 emitted, the only explanation for the difference in SO_2 emissions is error in the SO_2 analysis. The SO_2 was analyzed in this start-up using the Reich test. If the gas sample collected for the SO_2 analysis were insufficiently filtered it would contain quantities of ammonium bisulfite and ammonium sulfite particulate, that interferes with the SO_2 analysis producing a

TABLE 15

START-UP TEMPERATURE CONTACT ACID PLANT U_2 SINGLE ABSORPTION PLANT WITH AMMONIA SCRUBBER

		MASS A		MASS B		MASS C		MASS D			
Time	Boiler Exit	Entrance	Exit	Entrance	Exit	Entrance	Exit	Entrance	Exit	Inlet To Scrubber	Acid Inlet Temperature
6:00	503	629	810	760	734	738	684	714	490	130	
6:15	550	640	878	746	793	771	757	733	604	139	
6:30	563	684	955	773	845	822	828	775	738	142	159
6:45		710	1050	768	872	859	855	812	786	162	184
7:00	576	729	1118	742	975	880	878	833	793	162	184
7:15	590	760	1050	733	1000	900	975	878	846	180	197
7:30	602	781	993	762	878	843	1010	905	883	188	202
7:45	604	802	1090	822	803	795	983	908	926	195	208
8:00	609	814	1095	869	906	851	871	843	924	200	212
8:15	612	814	1116	868	916	882	849	806	884	203	215
8:30	615	819	1132	856	986	890	889	811	840	206	215
8:45	615	814	1147	852	982	883	926	856	856	204	208
9:00	619	812	1149	849	971	886	925	850	871	200	203

NOTE: ALL TEMPERATURES ARE IN °F

TABLE 16

AMMONIA SCRUBBER CONDITIONS AND EMISSIONS DURING ACID PLANT START-UP ON PLANT "U_2"

(COMINCO SCURBBER WITH MIST ELIMINATOR)

Time	Entrance to Converter % SO_2	Absorbing Tower Exit % SO_2	Effluent Outlet % SO_2
6:00 PM			.118
6:15	6.45	.278	
6:30		.34	.091
6:45	7.5	.255	
7:00		.255	.121
7:15	8.8	.24	
7:30		.245	.190
7:45	8.3	.255	
8:00		.33	.152
8:15	8.55	.33	
8:30		.255	.128
8:45	8.55	.18	
9:00		.205	.128
9:15	8.65	.21	
9:30		.185	.128
9:45	8.5	.19	
10:00		.235	.110
10:15	9.0	.183	
10:30			.103
10:45			
11:00			.094
11:15			
11:30			.110

An Example of a Single Absorption Plant "U_2" Entering and Leaving Malfunction Operating Conditions

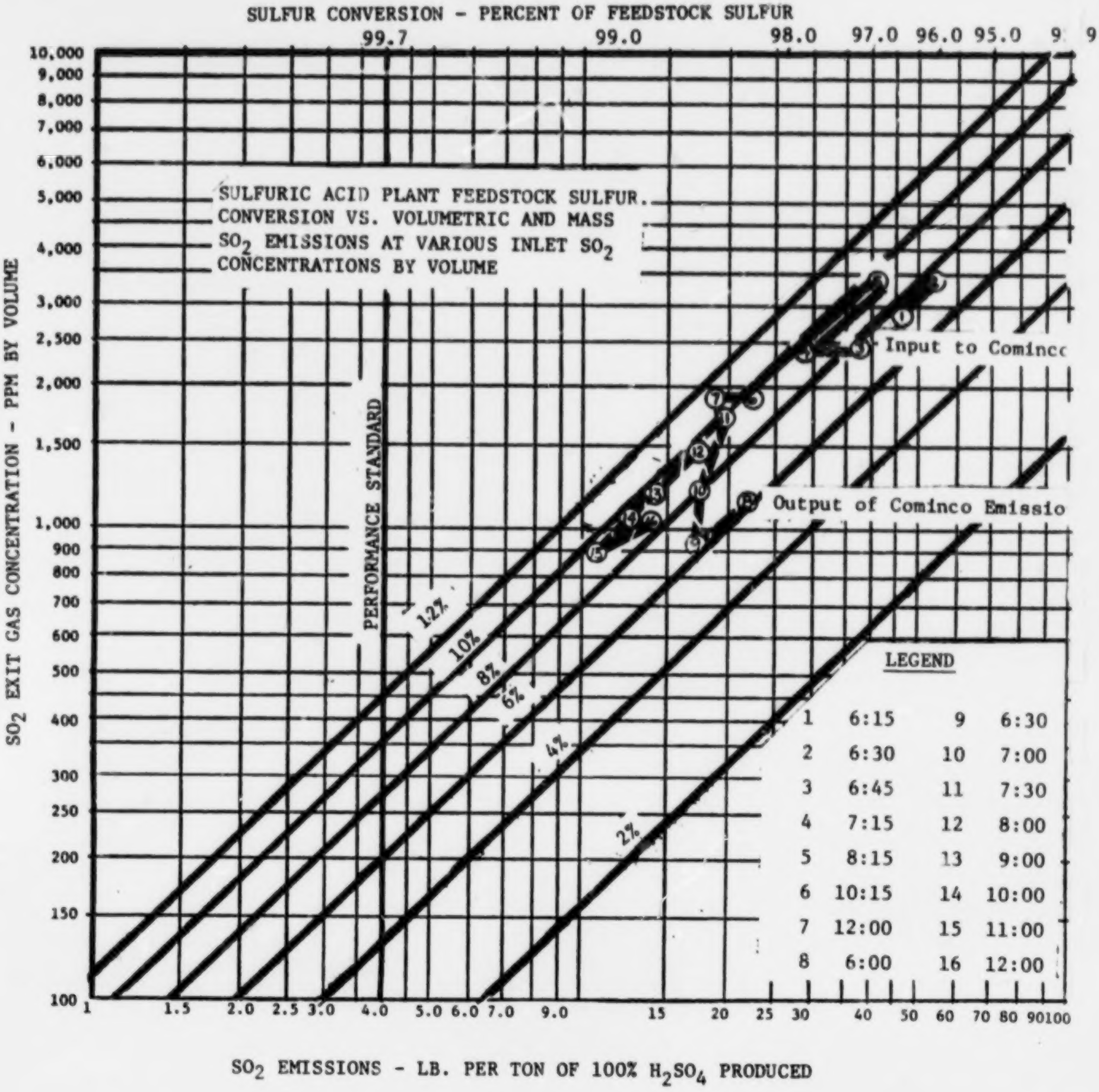


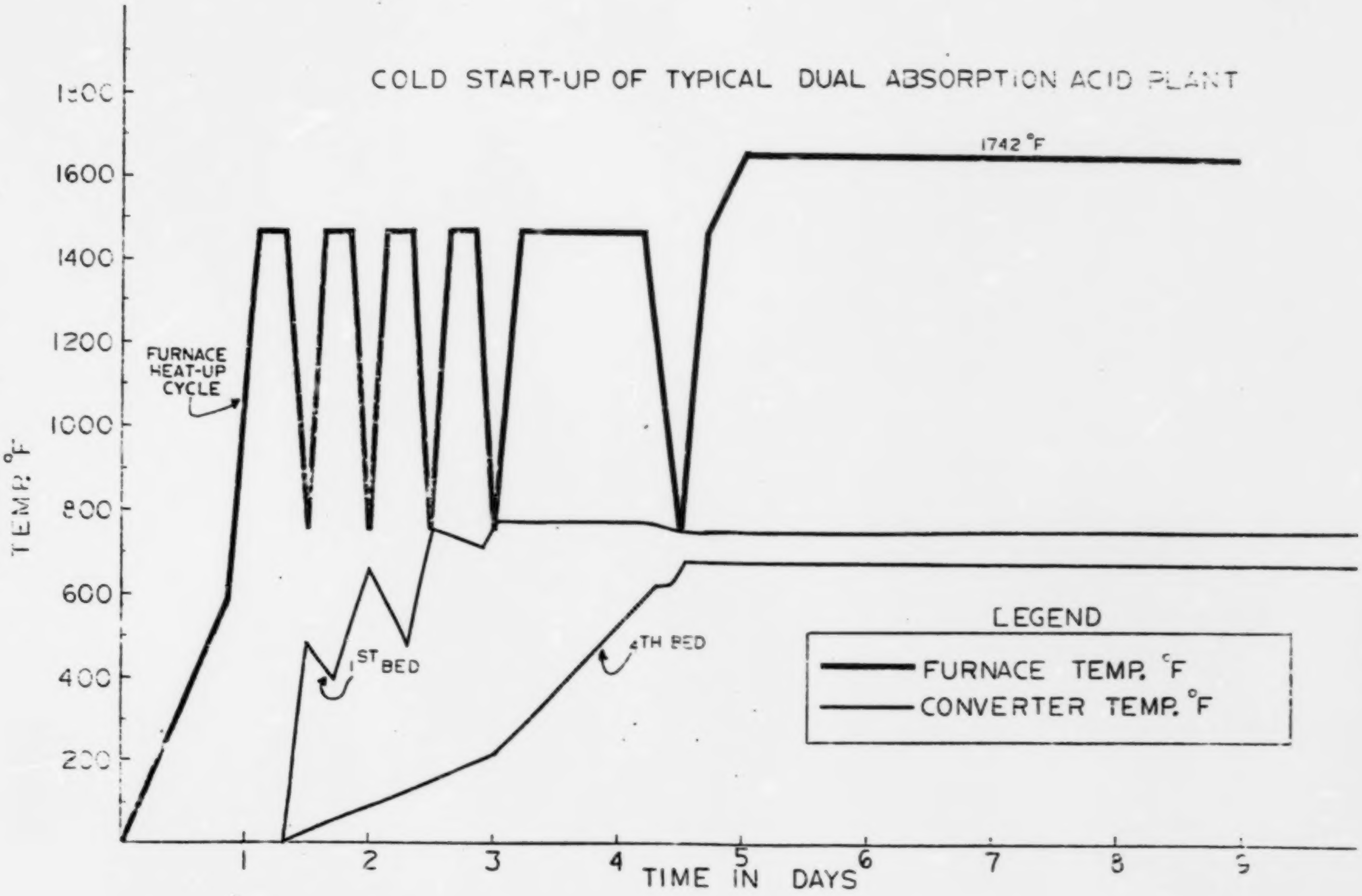
Figure 14

Note: Numbers represent clock time sequence.

higher result. This explanation for the high SO_2 emissions cannot be verified at this point, but appears to be the most logical explanation. In addition the SO_2 emissions from the scrubber from plant U_2 do not show the same degree of variations with changes in scrubber input SO_2 concentrations as seen in data from plant U_1. This fact may be an indication the particulate matter is masking the true SO_2 concentration in the vent gas.

Dual Absorption Plants

It has been previously stated that the dual absorption plants can be started up without exceeding SO_2 emissions by careful attention to procedures and process control, and if malfunctions of equipment and control instruments do not occur. This type of start-up, however, requires up to five days of preparation time, and process equipment and instrumentation do not always perform properly after a shutdown period. A preheat cycle for a dual absorption acid plant not equipped with auxiliary heaters is shown in Figure 15. During this preheat cycle all of the heat for preheating the converter is obtained by firing fuel in the sulfur furnace. Since the maximum temperature of the sulfur furnace is 1,500F, fuel must be burned in the furnace in a cyclic manner to prevent overheating the furnace. The off-on control of heating in the furnace permits adjustment of the heating rate of each catalyst bed. Because of the thermal lag throughout the converter, the first catalyst bed is heated in a cyclic manner reflecting the off-on cycles



COLD START-UP OF TYPICAL DUAL ABSORPTION ACID PLANT

Figure 15

in the furnace, while the fourth catalyst bed heats at a slow rate continuing for a period up to five days. If sulfur feed to the furnace is started before the fourth catalyst bed reaches operating temperature, incomplete conversion will take place in this bed causing high emissions of SO_2 from the absorber. Because of lost production resulting from the slow preheating procedure, preheat is often reduced and sulfur feed begun before proper temperature is obtained in the fourth bed. This is the primary cause of high SO_2 emissions from a sulfuric acid plant during the initial one to two hours of start-up operations. Once SO_2 is admitted to the converter the exothermic oxidation in the converter will quickly bring the catalyst bed to operating temperature, reducing the SO_2 emissions to a more normal level.

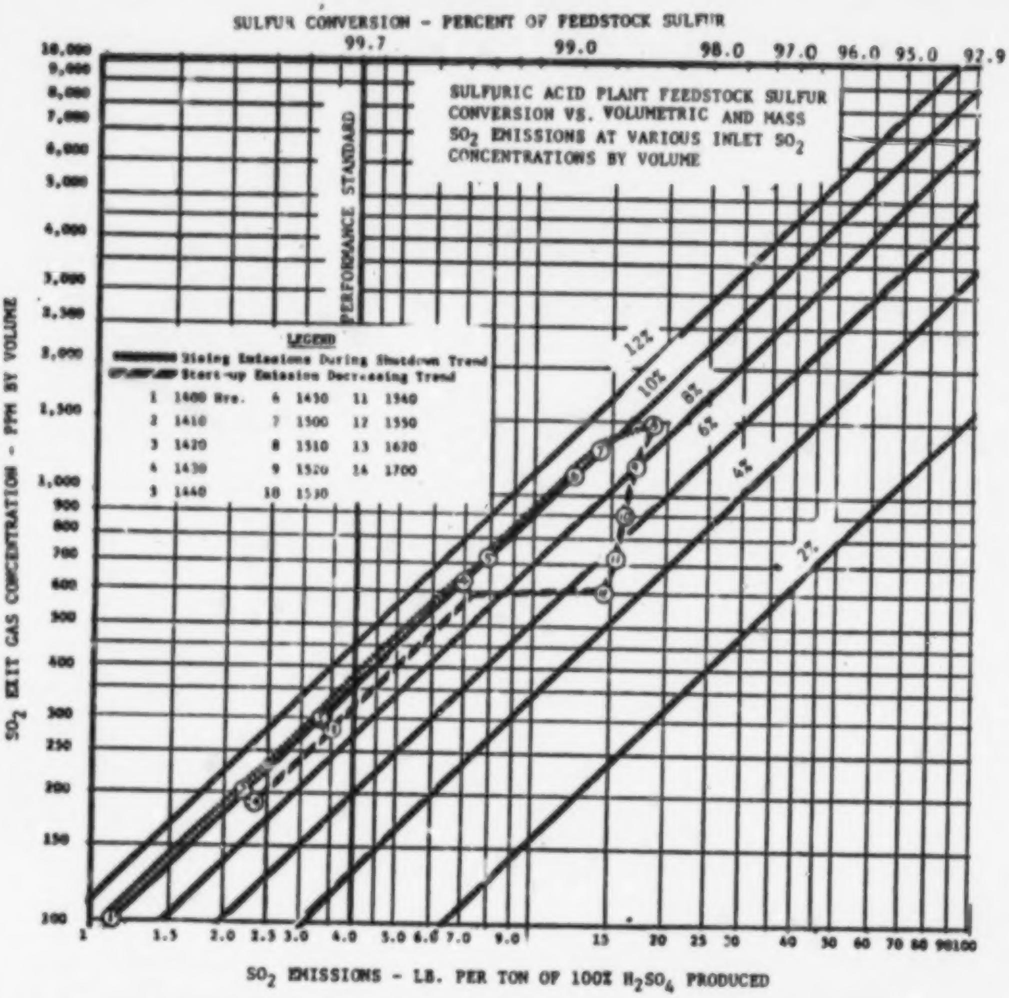
Another cause of high SO_2 emissions during start-up operations is operation of the sulfur furnace at full sulfur feed rates from the beginning of the start-up procedures and before catalyst bed temperatures have stabilized. These emissions on start-up can be reduced by initiating sulfur flow at reduced rates until proper operating temperatures in all catalyst beds have been obtained.

A typical dual absorption plant start-up will produce SO_2 emissions with a peak value of up to 3,000 ppm at one to two hours after start-up. Emissions will normally be in excess of performance standards for a period of two to four hours after the beginning of sulfur feed. This range and duration of emissions will normally occur during start-up operations following a shutdown period of more than four hours. This is primarily due to the lack of adequate preheating time when converter temperatures have fallen below permissible limits. These start-up relationships are shown in Figure 12, discussed in the previous section.

The complete history of SO_2 emissions for a dual absorption plant (Plant "Q") considered typical during start-up operations is shown in Figure 16. This curve indicates that the plant was started up with maximum SO_2 concentration feed to the absorber, with a peak SO_2 emission reached in approximately two hours after start-up began. At this point the sulfur feed concentration was reduced, causing the SO_2 emission to fall from 1,500 ppm to 600 ppm. The SO_2 feed concentration was again slowly increased as the converter stabilized, and emissions continued to drop to 200 ppm at normal SO_2 concentration in the feed. At this point the unit was operating at a total emission of 2.4 pounds per ton of H_2SO_4 produced.

An attempt was made to establish a statistical model for start-up emissions in terms of converter temperatures using data from plant "J" start-ups. A standard statistical analysis of these same thirteen data points was presented in Table 5B as compared to normal data. The regression analysis gave correlations that could not be considered significant, for the same reason discussed in the section on normal operating data. In addition, the inability of the catalyst masses to

An Example of a Dual Absorption Plant ("Q") Entering and Leaving Malfunction Operating Conditions--During Start-Up



Note: Number values represent clock time intervals from a stable steady-state dual absorption plant approaching excessive emissions and returning back to normal operating conditions within 1400-1740 or three hours 40 minutes time. Violation time less than two hours.

Figure 16

follow sudden changes in SO_2 inlet concentrations causes a displacement in the temperature--SO_2 emissions relationship during the transient conditions of start-up. An acceptable model of the catalyst operation during start-up must include factors involving this lag in conversion efficiency that could not be determined from the data avaiable.

The 13 data points considered in the regression analysis were also analyzed statistically for SO_2 emissions in terms of time after the beginning of start-up operations until 300 ppm SO_2 emissions is reached. It was calculated that the average period was 6.34 hours, with 95 percent of all start-up periods falling between 3.14 and 9.54 hours. These results were in agreement with the graphical data presented previously in this section. Details of the statistical analysis are included in Appendix "C".

MALFUNCTION CONDITIONS

Single Absorption Plants

Single absorption acid plants cannot meet performance standards for SO_2 emissions without the addition of vent gas cleaning systems. Acid mist emissions from single absorption plants are also frequently above the performance standards unless the plant is equipped with special means for eliminating this mist. Although single absorption plants are not specifically included in this study, data were obtained from two single absorption acid plants (Plant U_1 and U_2) for acid mist emissions when using both dark and bright sulfur. These data serve to illustrate the problems encountered when burning dark sulfur in a single absorption plant that is not equipped with appropriate filters to remove the acid mist. As illustrated on Figure 17, the emission of acid mist for dark sulfur feedstock is approximately three times that encountered with bright sulfur. The emissions from dual absorption acid plants equipped with normal mist eliminators is plotted on the same curve for comparison. The burning of dark sulfur in the modern dual absorption acid plant does not normally affect the acid mist emissions significantly, since these plants are equipped with efficient mist removal systems. The single absorption acid plants plotted on this figure are equipped with high efficiency Brink filters, and when these are in operation acid mist emissions are below performance standards.

The range for acid mist emissions for all plants studied, burning dark sulfur and bright sulfur, are shown in Figure 18. The plants described in Figure 17 fall within the range of all the plants studied.

A statistical study was made of Plants U_1 and U_2 in an effort to show the effect of catalyst aging on SO_2 emissions and acid mist. The results of the study for SO_2 emissions were inconclusive, since factors other than catalyst aging mask the change of SO_2 with time. One of the major causes of SO_2 variation in time was the introduction of dark sulfur into the unit during some periods of operation. The specific effect of dark sulfur on SO_2 emissions was not clear, however, since

Acid Mist Emission Average Operating Levels for Both Dual (Plant Q) and Single Absorption (Plant U_1 & U_2) Contact Acid Plants

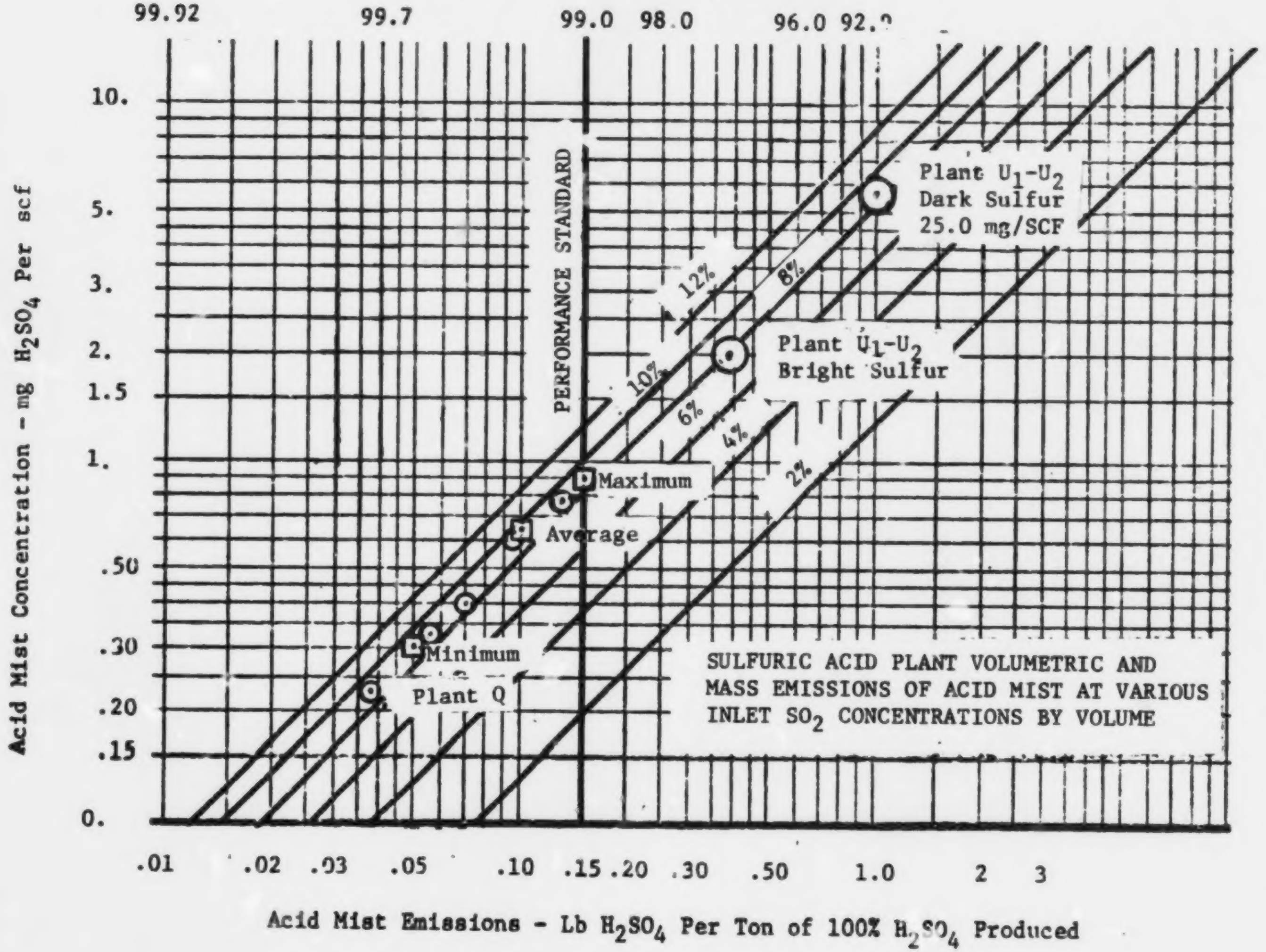


Figure 17

NORMAL RANGE OF OPERATION FOR ACID MIST EMISSIONS OF NEW DUAL ABSORPTION AND SINGLE ABSORPTION ACID PLANTS BURNING BRIGHT AND DARK SULFUR

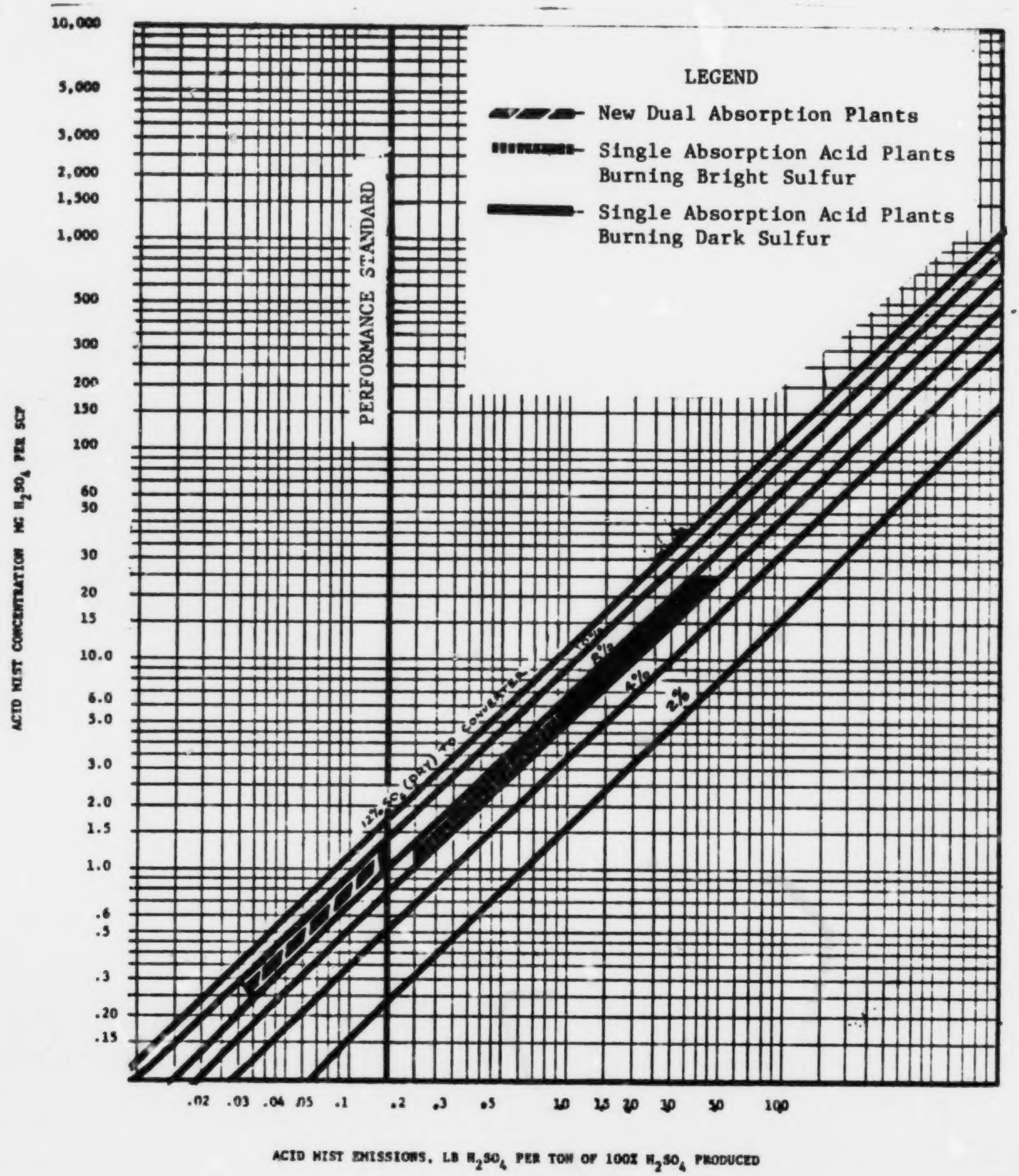


Figure 18

other factors were also involved. The effect on SO_2 emissions of catalyst aging probably cannot be determined using this type of evaluation, since the addition of new catalyst during each cleaning cycle will tend to replace the aged catalyst over a period of approximately 10 to 12 years, thus maintaining the overall activity of the catalyst bed at a point slightly below that of a new plant.

Correlation of operating time with acid mist for these plants however show a very significant change during the period when dark sulfur was being burned. When bright sulfur was burned a very constant acid mist emission rate was experienced. When dark sulfur was introduced to the plant the acid mist emissions increased (approximately 20 times) until the dark sulfur feed was discontinued and bright sulfur was again fed to the furnace. With the introduction of bright sulfur, acid mist immediately dropped to the normal level. A plot of the acid mist emissions with respect to time is shown in Figure 19.

Single Absorption Plants with Tail Gas Cleaning

Operating data were obtained from an extended period of operation from a single absorption acid plant burning bright sulfur and equipped with an ammonia scrubber. Three operating periods for this plant (Plant "K"), containing a series of malfunctions is shown in Figures 20, 21, and 22, A study of the total operating data from this plant indicates that the important operating parameters are scrubber gas flow, ammonia concentration in scrubber liquid, and scrubber liquid pH. In the opera-

COMPUTER PLOT OF ACID MIST VS. TIME

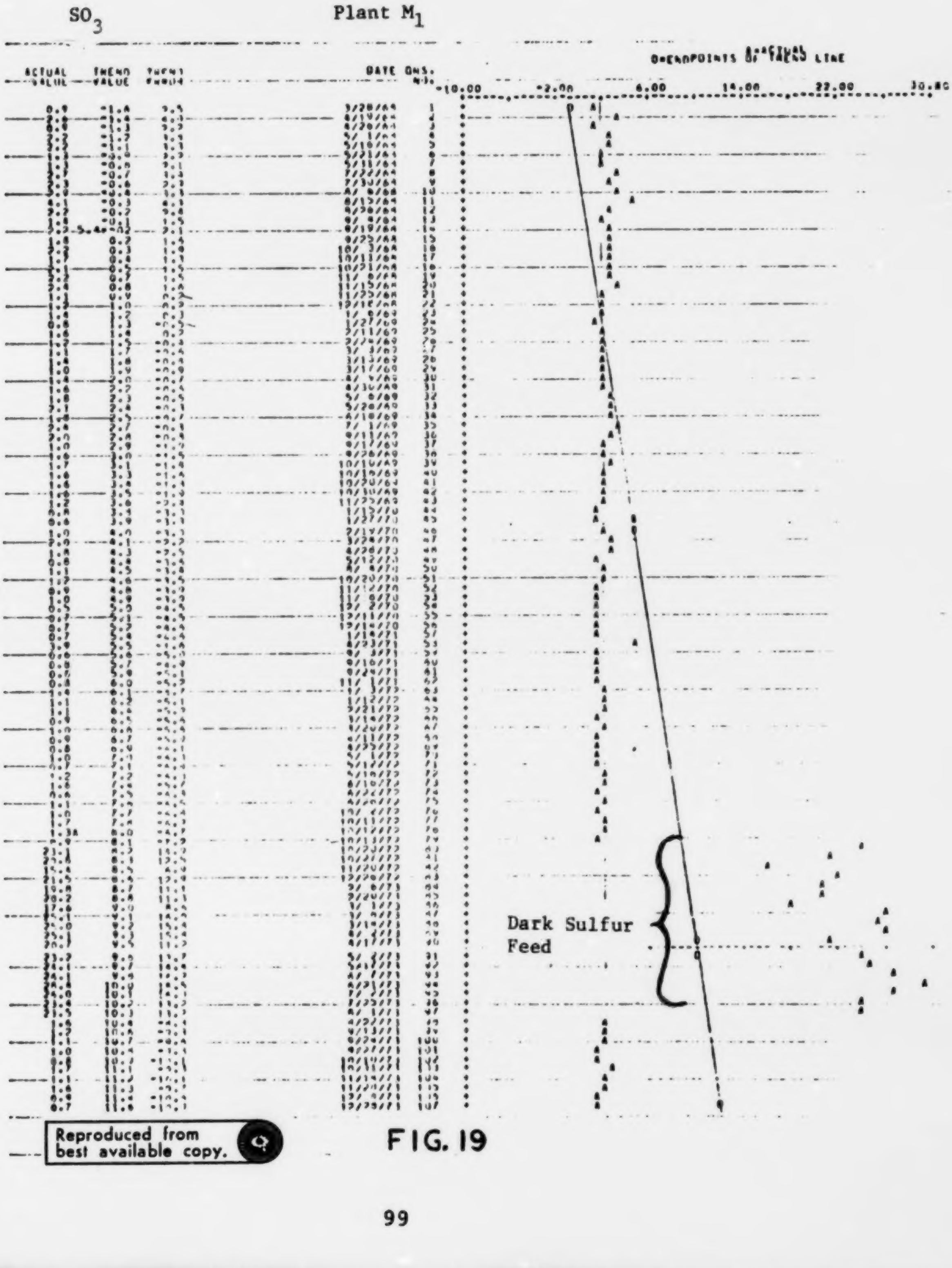


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FIG. 19

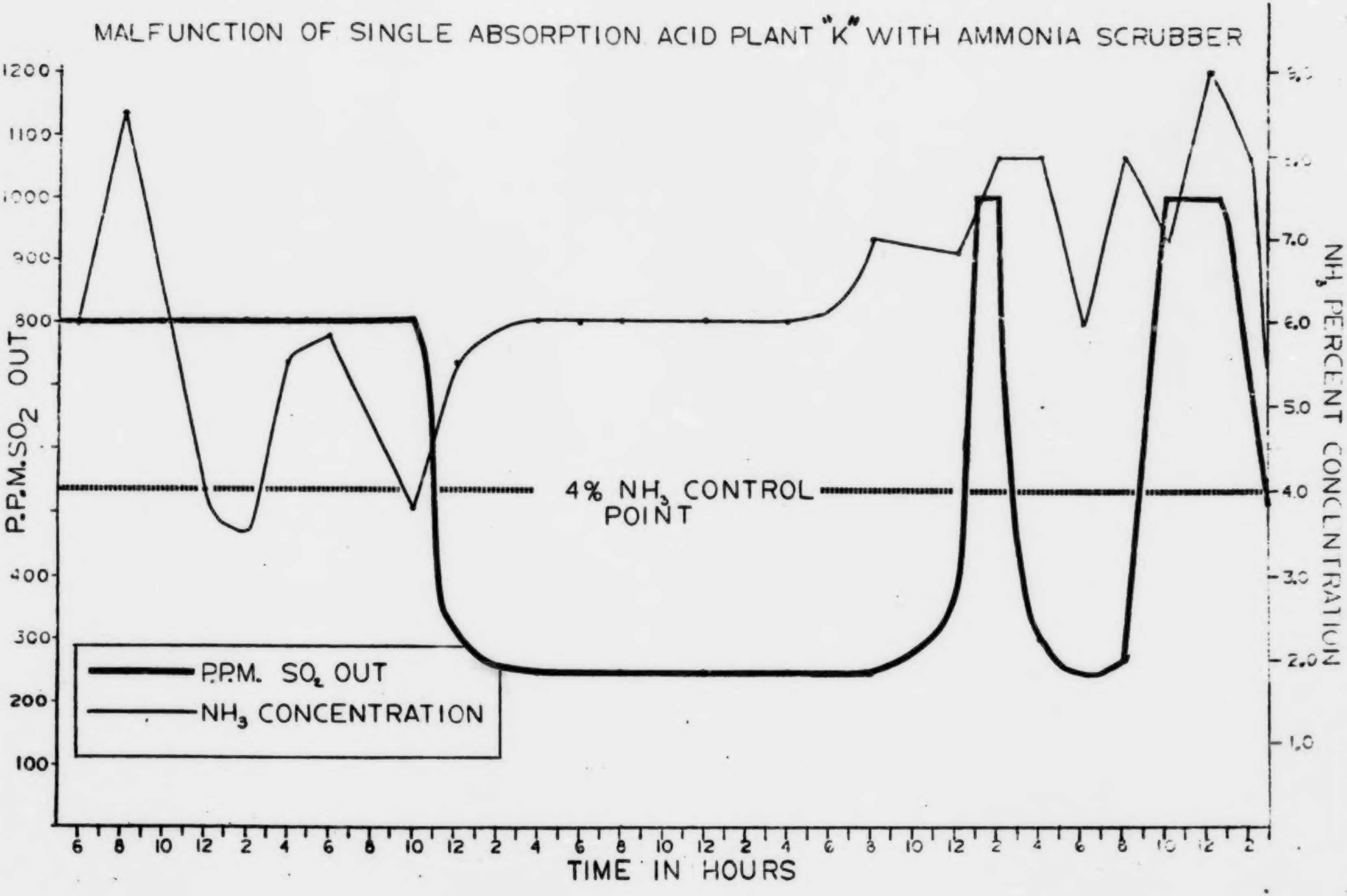

MALFUNCTION OF SINGLE ABSORPTION ACID PLANT "K" WITH AMMONIA SCRUBBER
P.P.M. SO2 OUT
1200
1100
1000
900
800
400
300
200
100
NH3 PERCENT CONCENTRATION
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
4% NH3 CONTROL POINT
P.P.M. SO2 OUT
NH3 CONCENTRATION
6 8 10 12 2 4 6 8 10 12 2 4 6 8 10 12 2 4 6 8 10 12 2 4 6 8 10 12 2
TIME IN HOURS

Figure 20

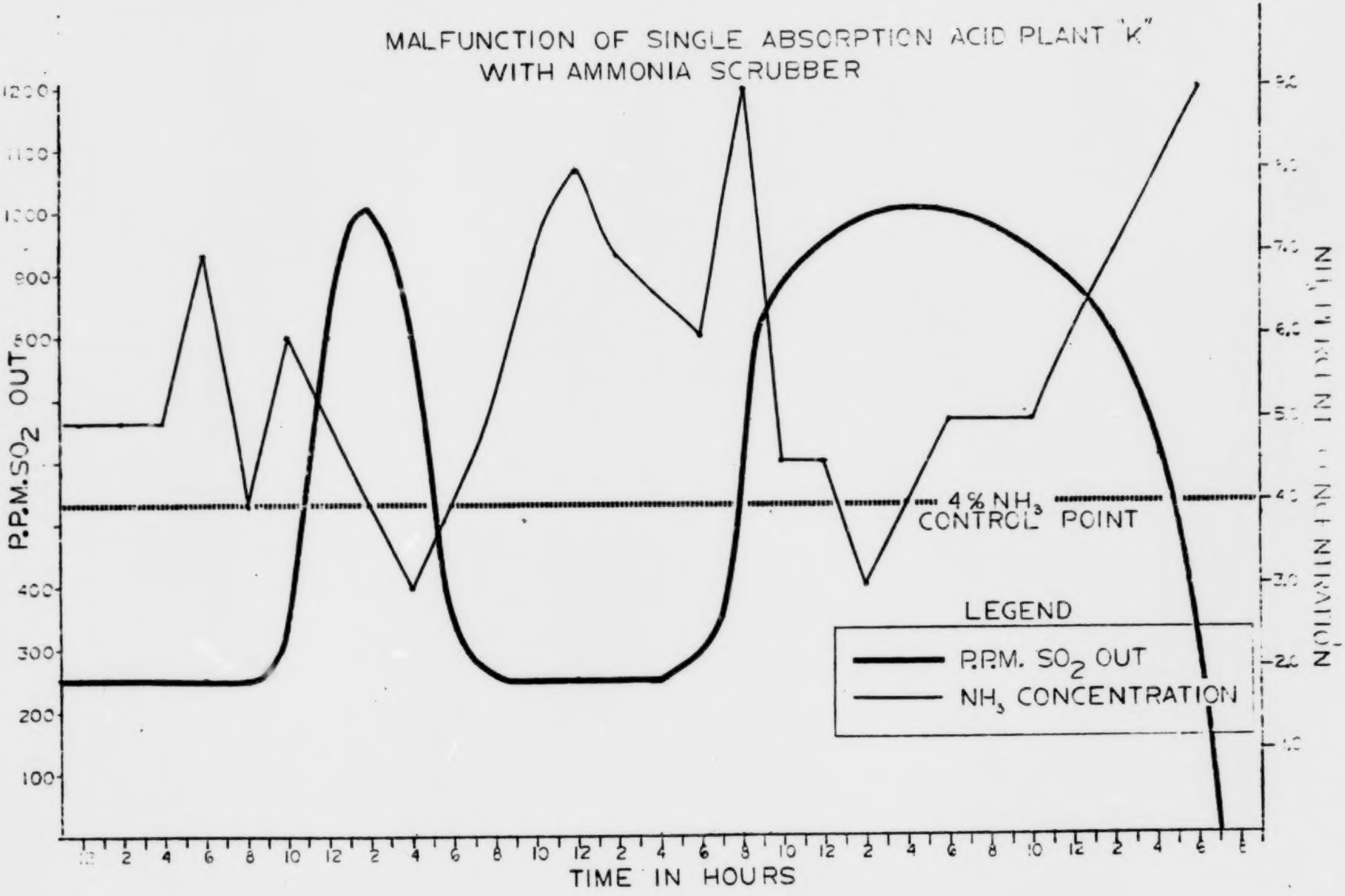
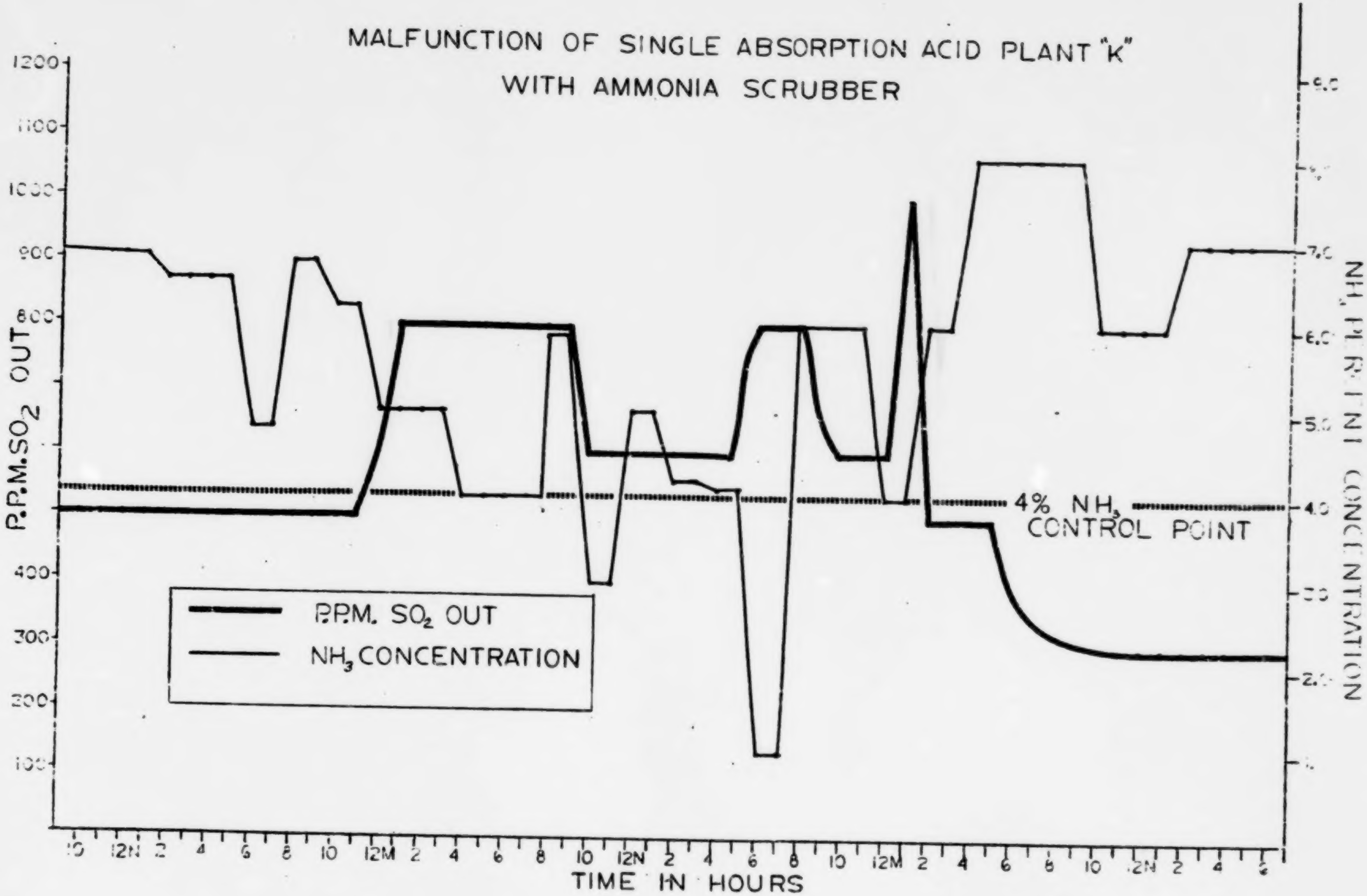

MALFUNCTION OF SINGLE ABSORPTION ACID PLANT "K"
WITH AMMONIA SCRUBBER
P.P.M. SO_2 OUT
1200
1100
1000
900
800
400
300
200
100
NH_3 PERCENT CONCENTRATION
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
4 % NH_3 CONTROL POINT
LEGEND
P.P.M. SO_2 OUT
NH_3 CONCENTRATION
12
2
4
6
8
10
12
2
4
6
8
10
12
2
4
6
8
10
12
2
4
6
8
10
12
2
4
6
8
TIME IN HOURS

Figure 21



MALFUNCTION OF SINGLE ABSORPTION ACID PLANT "K"
WITH AMMONIA SCRUBBER

Figure 22

tion of the plant observed, the last two parameters were generally related. Ammonia concentration was selected for plotting against sulfur dioxide emissions, with periods of abnormal gas flow noted on the graphs.

Figure 20 contains one period of 24 hours when SO_2 emissions were below 300 ppm. During this period of time the ammonia concentration was steady at six percent. Prior to this operation the ammonia concentration was out of control, generally running lower then six percent, causing the SO_2 emissions to maintain a constant 800 ppm. At the end of the stable operating period the flow through the scrubber was increased beyond the scrubber capacity for a short period, causing the SO_2 emissions to increase drastically from 300 ppm to approximately 1,000 ppm. During this time the ammonia concentration remained generally high but was unable to control the emission of SO_2 because of high gas flows resulting from high acid production. A reduction of gas flow for a short period again reduced the emissions to below 300 ppm, followed by another period of high gas flow with 1,000 ppm emissions. This curve shows the effect of exceeding the scrubber capacity for gas flow, resulting in a large increase in SO_2 emissions. Simply maintaining high concentrations of ammonia in the solution during these high gas flow periods will not maintain SO_2 emissions at the appropriate level.

Figure 21 further illustrates the effect of ammonia concentration on SO_2 emissions. During the initial part of this operating period the gas flow through the scrubber was below the normal level, permitting control of SO_2 at 250 ppm with an ammonia concentration of only five percent. When the ammonia concentration was lost because of ammonia evaporator problems, SO_2 momentarily increased to 1,000 ppm before the ammonia concentration was raised reducing the SO_2 emissions. Continued upset in the control of ammonia concentration eventually resulted in the shutdown of the unit.

In Figure 22 the ammonia scrubber was operating at a gas flow above its normal rates during the initial part of this period. During this 12 hour period the SO_2 emission was 500 ppm with an ammonia concentration of seven percent. Significant increases in the gas flow through the scrubber resulted in loss of ammonia concentration control, with the ammonia concentration dropping to the set point of four percent. During this period of time the SO_2 emissions increased to 800 ppm. This portion of the curve illustrates the inability of the scrubber to maintain SO_2 emissions at the 300 ppm level with an ammonia concentration equal to the four percent setpoint. After continuing upsets in flow rates and ammonia concentrations during the remainder of the two and a half day period shown on this curve, the ammonia concentration was again established at approximately seven percent, and with gas flow returned to normal, SO_2 emissions dropped below 300 ppm.

These three figures show the need for careful ammonia concentration control at a level of approximately seven percent and gas flow rates within the proper limits of scrubber design if SO_2 is to be maintained below the 300 ppm standard. Controlling the ammonia at a concentration of four percent will reduce the amount of ammonia consumed in the scrubber, but will always result in an emission level of approximately 800 ppm when gas flow rates are within design limits.

Data were collected on one single absorption acid plant equipped with a sodium scrubber. This plant is designated as Plant "Y". Figure 23 shows the response of the sodium scrubber to a sudden drop in gas flow rates through the scrubber. The design flow of this scrubber is 5,000 scfm but normal operation is set at 6,300 scfm. During the period of operation shown on the graph, the gas flow through the scrubber was dropped to 3,200 scfm causing the SO_2 emissions to drop from 940 ppm to 50 ppm. During this same interval the scrubbing solution temperature increased and the pH dropped slightly. These other parameter changes were primarily results of the drop in flow rates.

The sodium process is capable of reducing SO_2 in the vent gas to 250 ppm in normal operation, as demonstrated by EPA performance test. The data from plant "Y" indicates the high sensitivity of the process to flow rates, and the need to restrict gas flows to within design limits.

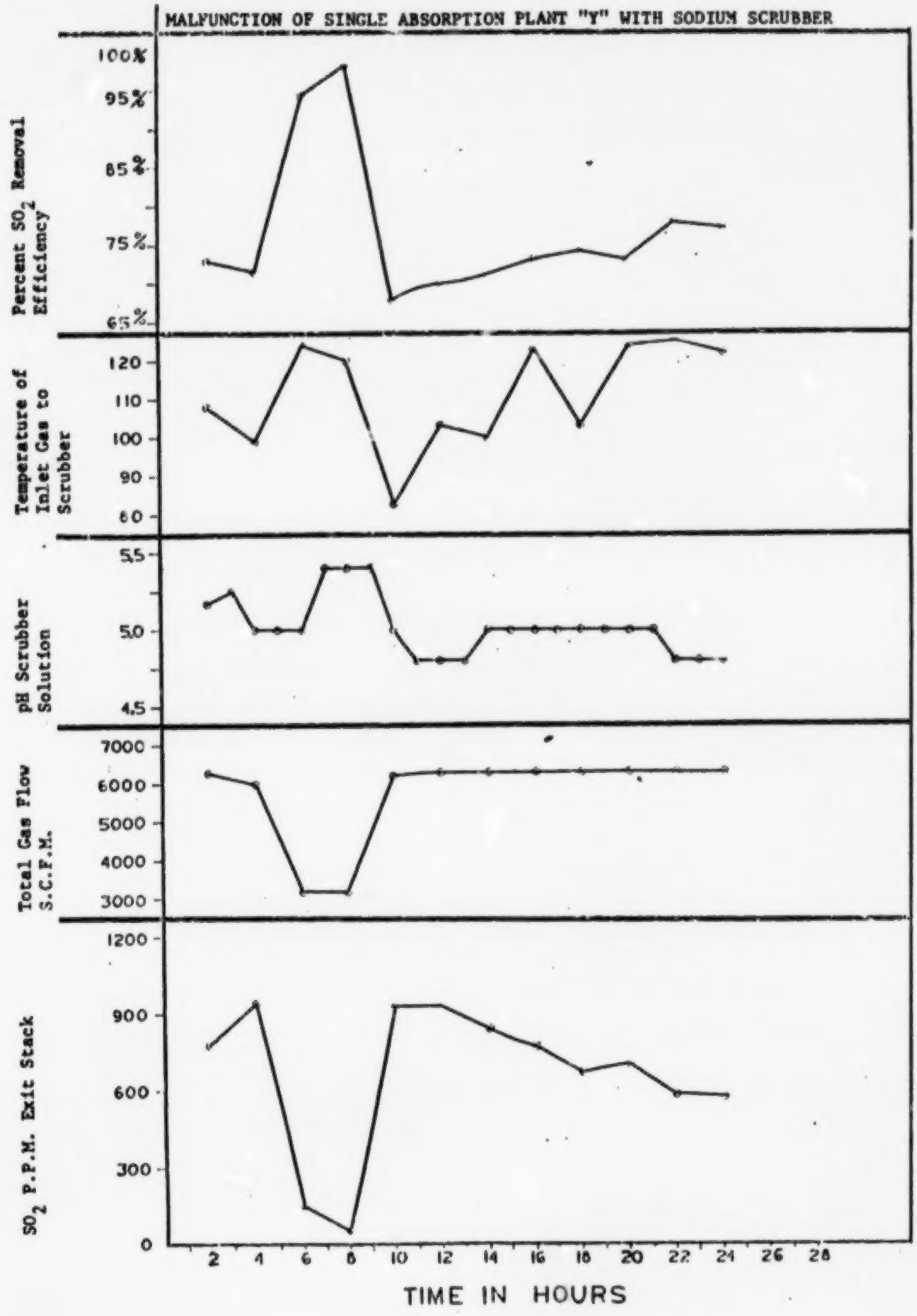

MALFUNCTION OF SINGLE ABSORPTION PLANT "Y" WITH SODIUM SCRUBBER
Percent SO_2 Removal Efficiency
100%
95%
85%
75%
65%
Temperature of Inlet Gas to Scrubber
120
110
100
90
80
pH Scrubber Solution
5.5
5.0
4.5
Total Gas Flow S.C.F.M.
7000
6000
5000
4000
3000
SO_2 P.P.M. Exit Stack
1200
900
600
300
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
TIME IN HOURS

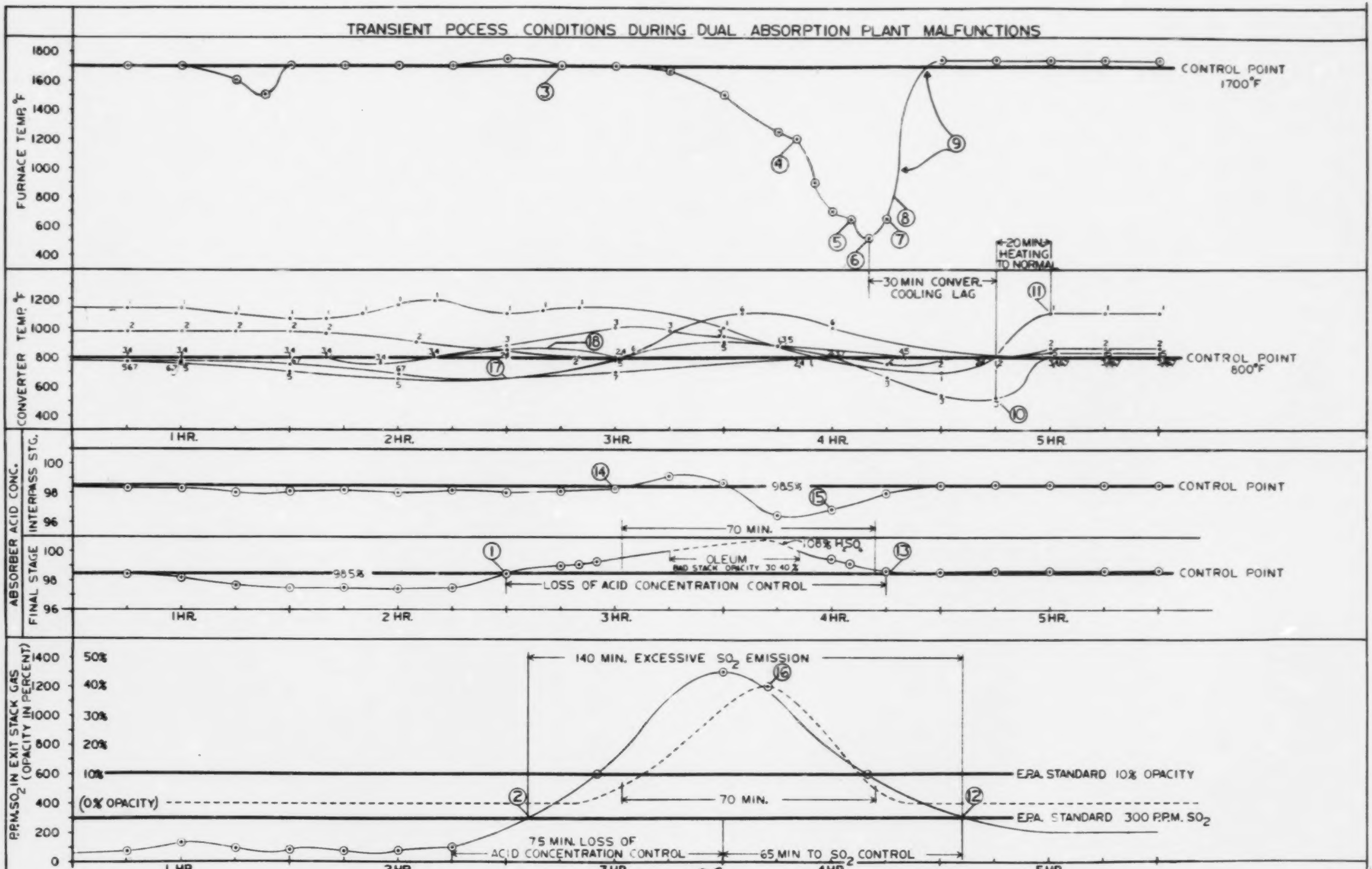
Figure 23

Dual Absorption Plants

A series of operating data for plant "Q" covering a five hour operating period is presented in Figure 24. Plant "Q" is a dual absorption acid plant burning bright sulfur, with a capacity of 1650 tons per day of 100 percent sulfuric acid. At the time the data were taken the plant was still in its shake down period after its initial start-up, and all the initial construction problems had not been eliminated. The five hour period shown contains a series of malfunctions affecting a variety of process parameters and causing excess emissions of SO_2 and acid mist.

The basic malfunctions that occurred were the loss of temperature control in the fourth bed of the converter, loss of dilution water to the acid tanks feeding the absorbers, and loss of sulfur flow to the sulfur furnace. The result of the combination of these malfunctions was an increase in SO_2 concentration from less than 100 ppm to a peak of 1,300 ppm and an increase in opacity from zero to 40 percent.

The sequence of events during the five hours of operation can be followed by referring to the large numbers of Figure 24, and is described in the legend on the second page of the figure. During the first hour of operation the plant was operating with normal emissions and with all parameters in normal range. At the one hour point temperature of the fourth bed of the converter began to show loss of control. This decrease in catalyst bed temperature began to change the SO_2 concentration


TRANSIENT POCESS CONDITIONS DURING DUAL ABSORPTION PLANT MALFUNCTIONS

TIME IN HOURS

FIG.24

FIGURE 24 (CONTINUED)

DESCRIPTION OF SIGNIFICANT OPERATING POINTS

Point No.	
1	Dilution water off with resulting rapid rise in H_2SO_4 concentration and SO_3 Emissions
2	Beginning of excessive SO_2 Emission due to loss of converter temperature control
3	Sulfur gun plugged
4	Loss of 50% sulfur flow
5	Loss of 75% sulfur flow
6	25% sulfur flow
7	50% sulfur flow
8	75% sulfur flow
9	100% sulfur flow
10	Temperature recovery point - start of conversion improvement
11	Stabilized converter bed temperatures
12	SO_2 Emissions back within EPA standard compliance due to stable converter temperature levels
13	98.5% H_2SO_4 concentration point at which high (30%-40%) opacity plume disappears
14	Dilution water malfunction
15	96.5% acid in final absorber - poor SO_3 absorption into high opacity plume
16	Opacity due to loss of H_2SO_4 concentration control
17	Subcooling of converter temperature
18	Lost 4th bed conversion because of interpass absorber failure

in the vent. The SO_2 concentration increased slowly at first, crossing the 300 ppm line at point 2. A short time after this point, dilution water flow to the acid pump tanks feeding the absorbers became inadequate causing the concentration of acid in the absorbers to increase. The concentration of acid to the primary absorber crossed the control point of 98.5 percent acid concentration at point 1. The increased acid concentration was seen in the final absorber at point 14. The reduction in dilution water flow resulted from a makeup water line of insufficient size to provide the required water. When the insufficient water flow became apparent from the control charts, water hoses were added to the pump tanks to dilute the acid and restore concentration control.

As the concentration of acid in the primary absorber began to increase the amount of SO_3 absorbed in the acid was reduced, increasing concentration of SO_3 in the fourth bed of the converter. This increased SO_3 reduced the efficiency of the fourth bed, causing an increase of SO_2 emissions from the vent. The result of this reduced conversion efficiency in the fourth bed is seen in the converter temperatures at point 18. As the SO_3 emitted from the stack began to increase, the opacity readings began to climb at about the third hour.

While the SO_2 emissions were increasing and the opacity was rising, the operators attempting to re-establish dilution water flow failed to notice the sulfur furnace temperatures were dropping. Low sulfur furnace temperatures resulted from the failure of one sulfur gun at point 3, reducing the flow by 25 percent, and the loss of a second sulfur gun at point 4, reducing the sulfur flow to 50 percent of normal. A third sulfur gun failed at point 5, leaving only 25 percent of normal sulfur flow at point 6 on the furnace temperature curve. During this period of loss of sulfur flow, two actions were occurring that partially counter-acted each other. The loss of SO_2 flow to the converter reduced the temperatures in the converter, which in turn reduced conversion efficiencies. During the same period the reduced SO_2 concentration in the feed reduced the need for conversion, permitting the excess SO_2 and unabsorbed SO_3 to be purged from the primary absorber and fourth catalyst bed. As the SO_3 was removed from the fourth catalyst bed the efficiency of this bed increased, reducing the amount of SO_2 emissions from the stack. The SO_2 emissions reduction begin at about 3.5 hours.

When the dilution water flow was re-established at point 15, opacity began to fall at point 16, reaching zero at point 13.

After it was determined that the three sulfur guns had failed, they were immediately restarted (at points 7, 8, and 9), restoring the flow of SO_2 to the converter and starting reheat of the catalyst beds. After re-establishing the sulfur flow the catalyst beds reached stable temperature at point 11, one half hour after starting the last sulfur gun. The short time required for recovery of normal converter temperatures illustrates the large heat imput from the SO_2-SO_3 reaction compared to the small heat loss (illustrated by the slow cooling of the converters when the flow of SO_2 to the converter was reduced). The SO_2 concentration from the stack reach 300 ppm at point 12, 4.5 hours into the operating period.

A very interesting sequence of events is presented in Figure 24, pointing up one of the major differences in operation between single absorption and dual absorption acid plants. In a single absorption plant, loss of dilution water to the absorber increases the SO_3 emission, causing acid mist, but does not appreciably change the SO_2 concentration in the vent stack. In a dual absorption plant however, loss of dilution water to the primary absorber reduces the absorption of SO_3, increasing the concentration in the fourth catalyst bed reducing its conversion efficiency. This will result in an SO_2 emission increase. Continued loss of dilution water, causing an increase in concentration of acid in the final absorber, results in high SO_3 emissions and increased opacity. In the case of the plant "Q" experience, an acid concentration of 108 percent is reached in the primary absorber and about 100 percent in the final absorber. It is also interesting that in the case of the operation of plant "Q" the SO_2 emissions from the plant decreased as the sulfur feed to the furnace was being lost and catalyst temperatures were falling. This sequence indicates the SO_2 emissions under the operating circumstances encountered in this event are more sensitive to SO_2 inlet concentrations than to catalyst temperatures. The curves also show the slow decrease in catalyst temperatures when sulfur is lost, and the very rapid increase in catalyst temperatures when sulfur flow is reinstated. It appears from this sequence of events that if loss of sulfur guns is detected sufficiently early to re-establish flows within a reasonable time, the converter temperatures can be re-established in a short period without causing excessive SO_2 emissions from the plant. Considering the size of Plant "Q", the transient conditions exhibited during this sequence of operations are surprisingly fast. This illustrates the need for close temperature and flow control of all the major process parameters.

SECTION VII

DISCUSSION

EMISSIONS DURING NORMAL OPERATION

The normal emissions for steady state operation of sulfuric acid plants consist of sulfur dioxide (SO_2), acid mist and opacity. Acid mist and opacity are related and under certain conditions, are different methods of measuring the same pollutant.

The SO_2 emission from a sulfuric acid plant results from a single cause. This cause is the inability of the catalyst in the converter to convert 100 percent of the SO_2 generated in the sulfur furnace into SO_3 for eventual absorption in the absorber. The effect of conversion efficiency is illustrated in Table 2, Page 41 of Section VI. Unconverted SO_2 is unaffected by passing through the absorber and is emitted with the vent gas.

The acid mist, on the other hand, can result from three different sources, all of which generate sulfuric acid, the ultimate form of the acid mist emitted. The most direct source of acid mist is carry-over of liquid particles of sulfuric acid from the top of the absorber. These particles range in size above three microns. A second source of acid mist emission is the formation of fine particles of sulfuric acid in the system by the reaction of SO_3 from the converter with water vapor contained in the gas. This water vapor is present because of insufficient drying of combustion gas or the generation of water vapor by the combustion of organic material contained in the sulfur. The effect of dark sulfur on emissions can be seen in Figure 17, Page 96 of Section VI. This source also produces sulfuric acid particles in the range of three microns and larger. The third source of acid mist emissions is the failure of the absorber to fully absorb all SO_3 fed to the bottom of the tower. Any SO_3 leaving the top of the absorption tower will immediately react with moisture in the ambient air to form very fine particles of sulfuric acid. These particles range in size below one micron.

Measurement of the opacity of the vent gas stream from a sulfuric acid plant is to a large extent the measure of the amount of sulfuric acid emitted from the process. Because of the fine particle nature of the acid mist and the effect of atmospheric conditions on the emissions, the measurement of opacity may be greater in one situation for the same amount of acid mist emitted than in another. Atmospheric effects on opacity may be seen in Table 7, Page 63 of Section VI. Acid mist resulting from acid carry-over from the absorber or reaction between SO_3 and water vapor in the absorber produces a dense white cloud in a cool, moist atmosphere, while the reaction of SO_3 gas and atmospheric moisture produces a blue cloud of a less dense nature. In addition to acid mist, the oxides of nitrogen (NO_x) may also contribute to opacity. The presence of NO_x and SO_2 in the gas stream produces acid mist by formation of a NO_x-SO_2 complex similar to the reaction in the chamber process. Nitrogen oxides are generated by combustion in the sulfur furnace or by the release of nitrogen oxides from combustion of organic material contained in the sulfur.

Steady State Emissions and Equipment Limits

As shown in Table 2, Page 41 of Section III a typical single absorption sulfuric acid plant emits SO_2 in a concentration between 1,500 and 4,000 ppm. This SO_2 concentration results from operation at normal design capacities depending upon the efficiencies of the converter to oxidize SO_2 to SO_3. The major variables influencing converter efficiency are the amount and condition of the catalyst contained in the converter. The catalyst becomes dirty with use and loses efficiency. Efficiency can be increased by cleaning. The cleaned and partially replaced catalyst will again perform at higher efficiencies; with proper cleaning and operation a catalyst bed will serve for a period of 15 to 20 years. During the cleaning process, six to ten percent of the catalyst is lost due to screening of the material in the first bed and must be replaced by new catalyst. The new catalyst is generally placed in the last bed and the catalyst from succeeding beds is used to replenish the material in the first bed. Misoperation of the converter or the use of sulfur containing large quantities of organic material can increase the deterioration rate of the catalyst. The effect of burning dark sulfur on catalyst activity is shown on Figure 19, Page 99 of Section VI.

The use of dirty sulfur feedstock will increase the frequency of cleaning of the catalyst as well as hasten the time of replacement. Overheating of catalyst to the range of 1200F will reduce useful life of the catalyst to three or four years. Careful operation and maintenance of the converter will assure SO_2 emissions in the range specified in the design of the plant.

The most important operational parameters effecting SO_2 emissions from a single absorption acid plant are the temperatures of the converter beds. Converter temperature ranges are shown in Table 4A, Page 51 of Section VI. Operation within a relatively narrow range of temperature for each bed is required to achieve optimum conversion. These temperatures are controlled by adjustment of by-pass dampers on the heat exchangers, by careful regulation of the SO_2 concentration in the feed gas to the converter, and the temperature of the sulfur furnace. The allowable range of converter temperatures is shown in Table 4C on page 56 of Section VI, Analysis of Process Variables and Emissions. Mean operating temperatures for the plant observed are also shown.

Each constructor of sulfuric acid plants employs individual details of design for the converter. These variations in converter design cause small variations in the efficiency of the catalyst and require different amounts of catalyst to obtain the appropriate conversion efficiencies. Some of the important design details in catalytic converters are the features reducing the wall effect or channeling of gas along the vessel wall, where contact with catalyst is reduced.

A very significant reduction in the SO_2 emission of sulfuric acid plants was achieved by the introduction of the dual absorption process in Europe approximately ten years ago. A dual absorption process is capable of reducing SO_2 emissions to a range between 100 and 300 parts per million. The process descriptions presented in Section IV detail the design of the dual absorption plant and the use of the primary absorber for increasing SO_2 conversion. Improved efficiency is also obtained by more careful control of temperatures in the converter and the use of higher catalysts loadings. Most of the process parameters in the dual absorption plant affect SO_2 emissions in the same manner as for the single absorption plant.

The use of vent gas cleaning systems in conjunction with single absorption sulfuric acid plants provides an alternate to the dual absorption sulfuric acid plants for reducing SO_2 emissions. Under normal steady-state operations a concentration of 250 parts per million of SO_2 is obtainable using the sodium scrubber system (Table 8, Page 66). Concentrations as low as 200 parts per million have been demonstrated by the ammonia scrubber system (Table 16, Page 93). The most efficient vent gas cleaning system studied is the molecular sieve system. This system will produce normal operating SO_2 concentration of less than 10 parts per million.

With any vent gas cleaning system, the concentration of SO_2 in the gas leaving the single absorption plant absorber influences the concentration of SO_2 in the vent gas from the cleaning system. However, this influence is not felt to the same extent as with a single absorption plant operating without a cleaning system. The buffering effect of the vent gas cleaning system somewhat reduces the effect of temperature control and the catalyst condition in the acid plant. With a vent gas cleaning system of sufficient capacity the single absorption plant can be operated up to 100 percent of the original capacity without excessive SO_2 emissions.

Operating parameters in the cleaning system, however, often strongly influence the concentration of SO_2 in the vent gas and become the primary parameters that must be controlled to maintain the concentrations within standards. In the sodium and ammonia alkali scrubbers, the most improtant process parameters are concentration and pH of the scrubbing fluid, temperature, and the liquid/gas ratio flowing through the absorber. These control points must be established for a specific scrubber design and must be maintained within narrow limits to insure proper SO_2 absorption.

The molecular sieve system is less sensitive to both SO_2 concentration in the input and other operating parameters. Sufficient detail is not available on the operating conditions of the system for a full analysis of the effect of process parameters. Because of the simplicity of the system the primary control of adsorption efficiency is the condition of the molecular sieve packing in the adsorption tower.

Acid mist resulting from carry-over of sulfuric acid from adsorption towers is controlled primarily by the installation of demisters in the outlet section of the absorber. In the case of the double absorption plant a demister is installed in the top of the primary absorber to reduce the carry-over of sulfuric acid into the converter bed and to protect the heat exhangers following the absorber. When properly equipped with demisters and operated to minimize generation of acid mist in the unit, the normal dual absorption acid plant will emit between three and 15 milligrams of sulfuric acid per standard cubic foot of vent gas. These concentration levels apply when burning clean elemental sulfur as feedstock. If dirty sulfur containing organics or acid sludges are burned, additional acid mist is generated within the process, seen in Figure 18, Page 97 of Section VI. Part of the acid mist will carry through the demisters, increasing the concentration of acid mist emitted. Most sulfuric acid plants constructed during the last ten years are equipped with appropriate demisters for controlling acid mist emissions. However some older single absorption plants still in operation cannot meet the standards because of lack of appropriate mist eliminator installation.

The liquid alkali vent gas cleaning systems cannot of themselves remove sufficient quantities of acid mist to permit standards to be met. When sodium or ammonia scrubbing systems are installed, demisters capable of reducing the acid mist carry over to within standards, must be installed before or after the scrubbers. In some cases a high energy venturi scrubber is operated in conjunction with the SO_2 vent gas absorber to eliminate the acid mist emissions.

Adsorption of acid mist as well as SO_2 gas is inherent in the nature of the molecular sieve vent gas cleaning system. With this system it is claimed no additional mist elimination equipment is required; however, data on the one plant evaluated to date indicate that the acid mist concentration before the molecular sieve adsorber will meet the standards without further cleanup and thus the claim cannot be verified as yet.

Since opacity in sulfuric acid plant vent stacks results primarily from acid mist, any of the previously discussed remedies for reducing acid mist will also reduce opacity. In addition to acid mist, NO_x is also a contributor to opacity. The presence of NO_x in the absorber feed will not only add a yellow color to the vent plume but will generate acid mist by formation of a complex between NO_x and SO_2 as in the chamber process. Proper operation of the furnace can reduce the NO_x generated from this source. However, if sulfur containing organics must be burned, more efficient filters are needed to remove the small sized particulate formed by reaction of water vapor and SO_2. Addition of high efficiency filters after the absorber of a single absorption plant will permit burning less expensive dark sulfur without excessive opacity.

Feedstock Changes

The effect of sulfur containing organic material has previously been discussed. In plants burning sludge acid a large variety of contaminants are encountered in the feedstock, making control of emissions from the plant difficult. Sulfur dioxide emissions vary with such feedstock because of the variability in the concentration of SO_2 fed to the converter. Sudden increases in the inlet SO_2 concentration increases the outlet SO_2. Because the operation of the sulfur furnace is more difficult, burning sludge acids can cause upset in the temperatures in the furnace, resulting in sublimation of sulfur and eventual deposition on the catalyst. A return to normal operating conditions will then oxidize the deposited sulfur greatly increasing the SO_2 load in the converter. This results in large concentrations of SO_2 over a short period of time in the plant vent stack.

With fresh catalyst in a dual absorption plant the design sulfur feed rate should not cause the SO_2 concentration in the stack to exceed the design limits. However as catalyst deteriorates or becomes dirty, feed rates must be reduced to maintain the acceptable concentration of SO_2 in the vent. Some modern plants are designed with sufficient catalyst to permit feed rates in excess of the design quantity when the catalyst is new and has maximum activity. The intention of the excess catalyst in such a plant is to provide for some deterioration of catalyst activity without exceeding emission standards at designed operating rates. Every effort must be made to control the feed rate and composition of the burner exit gas and conditions in the sulfur furnace as consistently as possible to reduce the possibility of SO_2 emissions.

Except in the case of dirty sulfur or sulfur containing organics the molten sulfur feed rate or sulfur furnace conditions do not appreciably effect the acid mist emissions from a plant adequately equipped with mist control equipment.

EPA PERFORMANCE TEST PARAMETERS

Federal regulations require that a performance test be run on a new or modified acid plant within a specified time after plant start-up and that periodic information be provided on operation of the plant after acceptance. These reports will include the stack emissions for SO_2, acid mist, and opacity. Certain process parameters are basic to determination of the emission rates and must be determined with sufficient accuracy to justify the reported figures. Table 3 in Section V is a summation of production plant data obtained in an EPA performance test.

Since emission rates are based upon tons of production of 100 percent acid per day, an acceptable method of measuring production rate must be provided. Either flow meters or storage tank levels are acceptable for measuring flow rate when properly confirmed by overall process material balances. If tank levels are used, arrangements must be made to isolate the tank from other product inputs or products outputs during the period of the test. If storage capacity is limited this isolation requirement may be a disadvantage in using this method of production measurement. If a flow meter is available for continuously measuring the flow of product, the readings from this meter can be used for establishing daily production rate. Appropriate calibration procedures must be followed to assure accuracy of the meter, and periodic test must be run to prove this accuracy. With either production rate measurement method, analysis of the product must be performed on a periodic basis to permit calculation of production on the 100 percent sulfuric acid basis.

During the initial performance test of a new acid plant, stack gas analysis is normally run using the standard EPA impingement train methods to establish the gas density, gas velocity, and concentration of SO_2 and acid mist. In order for this test to be performed, proper sample points must be installed in the stack in compliance with the regulation. Some acid plant designs have provided stacks of insufficient height to obtain the necessary lengths of straight run before and after the sample points to permit compliance with this test procedure. Full compliance with sample point configuration must be assured for the performance test or any follow up testing that must be done using the standard EPA methods.

The regulations also require a continuous SO_2 monitor installed on the vent stack. The instrument most commonly applied at this time is the DuPont model 460 analyzer. Data obtained from plants using this instrument indicate that the SO_2 concentration readings are reliable if the instrument is properly maintained. Improper installation and maintenance of this instrument however, can cause erroneous results, generally in the direction of low concentration measurements. If maintenance records are kept on this instrument a better evaluation of its performance can be obtained.

A variety of instruments using the principle of light transmission have been used for measurement of opacity in sulfuric acid vent stacks. These instruments generally appear to have difficulty in maintaining reliable operation, and visual comparison of the opacity of the vent gases is normally relied upon. Since visual opacity estimates include water vapor contained in the stack gases, complete analysis of the gases including sulfuric acid mist must be available before corrected opacity measurements can be obtained.

The only reliable methods available for obtaining acid mist concentration in the vent stacks are the impinger analysis methods. Since these test are difficult and time consuming, requiring two hours to run, they are not normally run in routine operation. Most plant operators will use visual measurement of opacity as an indicator of possible problems with acid mist emissions. When visual opacity estimates indicate the possibility of the presence of excess acid mist the impinger tests are run on the stack to provide information necessary for correcting the problem. Impinger tests must also be run during any period of special performance test and evaluation required by EPA.

SHUTDOWN EMISSIONS

Most plant shutdowns can be classified as either planned or unplanned shutdowns. The shutdowns resulting from catastrophic failure are beyond our concern in this study. Shutdowns can further be classified by short term or long term depending upon the length of time the plant is expected to be shut down. For purposes of our discussions a short term shutdown can be considered as one lasting less than four hours and a long term shutdown as one lasting more than four hours. When a planned shutdown is properly handled no excess emissions should be experienced from the sulfuric acid plant. The primary importance of shutdown method used is the effect of the shutdown on the subsequent start-up emissions. A properly prepared plant, shutdown for four hours or less, can be restarted without reheating the plant equipment. Figure 12, Page 76 of Section VII shows SO_2 emissions from a dual absorption plant during start-up after shutdown of various durations. If the shutdown extends for more than four hours, reheat of plant equipment is required to minimize emissions on start-up.

Planned Shutdown

The most important feature of a planned shutdown is preparation of the plant for eventual start-up to minimize start-up emissions. The first action in preparing for a planned shutdown is to have available a supply of strong acid for a transfer to the absorber and the drying tower. This increase in acid strength will help to offset the effect of moisture leakage into the plant and the accumulation of excess moisture resulting in dilution of the acid during the start-up operation. Stronger acid in the absorber and drying tower during startup will reduce the acid mist emissions from the plant.

After the plant is prepared for shutdown by increasing the concentration of the acid, the sulfur feed to the furnace is simply shut off and the generation of sulfur dioxide stopped. After a very few minutes of continued air flow to remove excess SO_2 from the furnace and move SO_3 from the converter to the absorber the air supply is shutoff and the dampers isolating the heat exchangers and converter are closed. The closed dampers will help to reduce the influx of humid air and conserve heat contained in the equipment. With normal heat losses from the plant, four hours downtime should not reduce the temperature below the point for start-up without preheat.

If the plant shutdown will extend for a prolonged period and maintenance must be performed on the process equipment, the unit must be cooled sufficiently to permit entrance. With this type of shutdown, air flow through the system is continued until all SO_2 is transported from the furnace to the converter and all SO_3 is removed from the converter to the absorber to make sulfuric acid. After most of the SO_3 has been stripped from the catalyst and transported to the absorber, the drying tower is bypassed to prevent dilution of the drying acid that would make start-up more difficult. The undried air containing very small quantities of SO_3 is vented to the atmosphere until the converter temperatures approach a dew point of approximately 100C. At this temperature dry air is again introduced to the system to prevent condensation of moisture and formation of sulfuric acid in the equipment, causing excess corrosion. The dried air containing the residual amounts of SO_3 is again vented to the atmosphere until the converter has reached the desired temperature. If only the furnace and the waste heat boiler must be cooled, undried air can be used for cooling if it is vented before entering the converter.

Unplanned Shutdown and Equipment Malfunctions

Many problems can arise in a contact sulfuric acid plant that cause emissions in excess of standards and often require an unplanned shutdown. Only a few of the major causes of shutdown are discussed here. Related shutdown causes can be grouped together in the following sections:

1. Sulfur feed system (Figure 24)
2. Combustion air (Figure 24)
3. Heat exchanger and converter temperature control (Figure 24)
4. Absorber and strong acid systems (Figure 24)
5. Vent gas cleanup systems (Figures 20, 21, 22, and 23)

One of the most frequent causes for unplanned shutdown is failure of the molten sulfur pumps and burners. When sulfur pumps or burners are lost and the SO_2 to the converter is reduced, excess emissions from the absorber do not necessarily occur. If the flow of sulfur can be reinstated before the converter temperatures have dropped below the acceptable range, the SO_2 converter efficiency can be maintained and SO_2 emissions controlled within limits. However if the converter temperature drops below 750F, the converter efficiencies decrease as the temperatures decrease and emissions increase when flow of molten sulfur is reinstated. A complete sequence of plant operation following loss of sulfur feed is shown in Figure 24, Page 108 of Section VI.

The combustion air blower in a sulfuric acid plant is one of the most critical items in the plant. This blower is normally driven by a steam turbine supplied with steam from the waste heat boiler. The speed of the air blower is controlled to provide sufficient air for complete combustion of the sulfur to sulfur dioxide and dilution air for subsequent catalytic oxidation of the sulfur dioxide to sulfur trioxide. If insufficient air is provided by the blower because of malfunctions of the blower control system or operation below the normal operating speed, incomplete conversion of SO_2 to SO_3 will take place in the converter. Failure to supply sufficient air to the system is probably the most frequent cause of excessive SO_2 emissions in sulfuric acid plants. When the air supply is dropped further, insufficient air is available for the combustion of sulfur to SO_2. In this situation the high temperatures in the sulfur furnace cause sublimation of sulfur and subsequent redepositing of sulfur in the catalytic converter.

Since the deposition of sulfur in the converter takes place during periods of low temperatures, resulting from insufficient sulfur combustion, a return to normal operating temperatures will oxidize the sulfur providing a large increase in the concentration of sulfur dioxide in the converter. This situation results in a large increase in SO_2 emissions from the plant. An added danger of subliming sulfur in the furnace is the deposition of the sulfur on boiler tubes causing failure of the tubes. Failure is caused by the burning of sulfur on the tube surface, resulting in localized melting of the tubes.

If the combustion air blower shuts down suddenly removing the flow of air to the furnace, no transfer medium will be available for sweeping the excess SO_2 and SO_3 from the system. In these situations higher levels of emissions will occur during the subsequent start-up operation.

The control of acid mist emissions depends upon feeding dry air to the sulfuric acid system to prevent reaction of SO_3 and water vapor to form the acid mist. If the concentration of acid in the drying tower drops below the operating limits, or if the quantity is reduced below that required by the air passing through the tower, excessive acid mist emissions will occur. This situation is usually detected first by the appearance of a heavy white plume from the vent stack.

Heat exchangers in sulfuric acid plants are subject to excesssive corrosion because of the presence of sulfuric acid and high temperatures. If a leak occurs in a water cooled heat exchanger the addition of water to the SO_2-SO_3 system results in a dense white plume of steam and sulfuric acid emerging from the vent stack. This situation will require a plant shutdown and excessive acid mist emissions will occur during the period of operation while the plant is being shutdown.

In a dual absorption plant using gas-to-gas heat exchangers, a leak in a heat exchanger can result in gas with a high concentration of SO_2 by-passing a portion of the converter catalyst beds. When this occurs the third or fourth catalyst bed can be overloaded with SO_2 and the concentration of SO_2 from the vent stack will increase. With this type of failure the plant must be shut down for repairs and excessive SO_2 will occur until the plant is completely purged of SO_2.

Failure of temperature control systems for the converter is one of the most minor malfunctions in terms of hardware but can be a major cause of excessive SO_2 emissions. Many of the older plants relied heavily on manually adjusted dampers bypassing the heat exchangers to regulate the inlet and outlet temperatures of the catalyst beds. Most modern acid plants depend more heavily on automatic control, introducing the possibility of temperature control failure. In most cases the significant temperatures in the converter are recorded on a multipoint recorder that gives a profile of the temperatures across the converter beds, providing a powerful tool for trouble shooting temperature control problems. If such a failure occurs manual control can usually be assumed to return the temperatures to proper operating points. Emissions resulting from this type of failure should not last long since the cause is easily corrected.

Plant shutdowns resulting from failures in the absorber system generally will arise from failure of the concentrated acid pumps supplying scrubbing acid to the absorber. If the concentration of the strong acid flowing to the absorber is reduced below operating requirements, SO_3 gas will be emitted from the absorber because of the inability of the lower concentration acid to absorb the SO_3. This reduced absorption results from the increase in surface tension of the low concentration acid, reducing the transfer of SO_3 into the absorber liquid. If the concentration of the absorber acid becomes too high the emissions of SO_3 will also increase because the reduced solubility of SO_3 in acid with concentration above 99.2 percent will increase the amount of SO_2 emitted. The effect of absorber acid concentration on SO_3 emissions is shown very graphically in Figure 24 of Section VII for both the primary and secondary absorber. Temperature of the absorbing acid must be maintained between 185F and 212F to maintain the vapor pressure of the sulfuric acid sufficently low to permit absorption of the SO_3.

Efficient absorption of SO_3 and sulfuric acid in the absorption tower requires good distribution of the acid flow down the tower and intimate contact with the SO_3 gases flowing up the column. If the volume of acid fed to the column is reduced, distribution of liquid in the column will be uneven and incomplete absorption results. Also, there is a risk of increasing the acid concentration in the tower beyond the 99.2 percent, thus producing SO_3 emissions. Complete failure of the concentrated acid pump feeding the absorber will result in immediate shutdown of the plant and large concentrations of SO_3 emissions for a short period of time until the SO_3 content of the plant has been vented.

All modern sulfuric acid plant absorption towers are equipped with a knitted wire mesh demister in the top of the absorption tower. In normal operation this demister collects most of the entrained acid particulates and prevents them from being carried into the vent gas stream. If this demister becomes partially plugged for any reason, the velocity of gas flow through the remaining portion of the demister will be too high to permit collection of the acid mist in the demister. This acid mist will be carried through the demister and emitted from the vent stack as entrained acid mist.

Vent gas cleaning systems are subject to many of the same problems affecting acid absorbers. The proper liquid/gas ratio in the absorber must be maintained to assure high absorption efficiency. If the flow of liquid is reduced or the flow of gas is increased beyond normal operating ranges, poor absorption of SO_2 will take place and SO_2 emissions will increase.

The alkali scrubber systems operate with close pH control on the absorbing solution flowing down the column. If the control system fails and the pH is allowed to deviate from the established range, poor absorption of the SO_2 from the tail-gas will result. In the case of the ammonia scrubber an excessive amount of sub-micron particulates of ammonium sulfite will be generated, possibly overloading the packed bed filter (Brink) normally installed to eliminate particulate emissions from the ammonia scrubber. Plants have been observed in operation where the Brink separators were plugged or the booster blowers for transporting the gases through the Brink separators were inoperative. When the filter system was bypassed a large cloud of particulate matter was emitted from the ammonia scrubber. The emission is not classified as acid mist but is objectionable none the less and must be controlled to meet opacity standards.

Cooling water is used in a sulfuric acid plant for cooling product and recirculating acid streams. Failure or cooling water in these systems will permit the acid temperatures to rise beyond the range of satisfactory operation resulting in various amoutns of acid vapors being emitted from the process. These emissions may occur from storage tanks or other areas where the hot acid is accumulated rather than from the vent gas stack.

The failure or impropoer operation of many other small pieces of equipment will cause similar problems in operation of the plant increasing emissions. Most of these, however, will fall into the same categories as those discussed and result in the same type of situations occurring.

Emissions from Misoperation of Plant

Frequently, high emissions from the acid plants result from misoperation of the plant. One of the major reasons for emissions is an attempt to operate the plant at a production rate higher than permitted by the amount or condition of the catalyst. Full recognition of the condition of the catalyst and its reduced capacity due to ageing must regulate the amount of production expected from the plant. If more production is demanded than is permitted by catalyst condition, excessive SO_2 emissions will occur.

In some cases it is necessary to burn sulfur containing quantities of organic matter. Burning this sulfur will cause emissions above the established limits, that may not be controllable with the existing plant equipment under any operating conditions. The only solution for eliminating these emissions is to prefilter the sulfur to remove the organic material or to obtain a supply of pure sulfur.

Improper attention to control of catalyst temperatures is one of the most common causes of excessive SO_2 emissions, but also one of the easiest problems to solve. Careful and constant operator attention to this control area will greatly reduce the probability of SO_2 emissions.

Both laboratory and process instrumentation information is available to assist in controlling the acid concentration and temperature in the absorber and drying towers. These process parameters are normally easy to control with proper attention and must be kept within proper range if acid mist standards are to be maintained.

Improper attention to or misadjustment of many of the process parameters in acid plants or vent gas cleaning systems will cause one or more of the plant pollutants to exceed standards. Careful and skillful control of the process at all times is required to comply with regulations.

START-UP PROCEDURES

Contact sulfuric acid plant start-up can be classified into three categories. These are initial plant or new catalyst, hot start-up after short term shutdown, and cold start-up after long term shutdown. Each type of start-up will require a particular start-up procedure to compensate for the conditions existing in the plant. The start-up procedure applied to the plant will also depend upon the availability of start-up heaters in the equipment and upon the availability of an associated sulfuric acid plant to provide the required heat and concentrated acid.

New Plant and New Catalyst Start-Up

When a new sulfuric acid plant is constructed the catalyst is received packed in polyethylene bags to prevent adsorption of excessive atmsopheric moisture. During installation of catalyst in the converter, however, considerable atmospheric moisture is adsorbed in the catalyst, requiring predrying of the catalyst bed before introduction of sulfur dioxide into the converter. During the start-up procedure the catalyst must also be activated to complete the reaction of the catalyst and sulfur to provide maximum activity.

The initial operation in the start-up procedure(10) is to pass hot air at approximately 250F through the catalyst bed at such a rate to permit increase in catalyst temperature at a rate of 50°F per hour. This air is dried by passing through the air drying tower. The flow of dry air through the catalyst is continued until the temperature has been increased in the catalyst beds to approximately 357F and the inlet and outlet bed temperatures are approximately equal, indicating the catalyst is now dry. After the catalyst is dry, heating is continued until the first catalyst bed inlet temperature reaches 825F. At this temperature the catalyst is capable of converting SO_2 to SO_3. Sulfur feed to the furnace is started at a low rate to provide low concentrations of SO_2 flowing through the converter. A low concentration of SO_2 is required to limit the maximum temperature in the catalyst bed to below 1,000F. Temperatures not exceeding 1150F must be maintained to prevent damage to the catalyst. Control of these maximum temperatures in the first catalyst stage will provide lower temperatures in the succeeding stages.

The SO_2 concentration should be gradually increased, maintaining these maximum temperatures, until full sulfur input rates are achieved. The total activation period for new catalyst will range between two and three weeks. The SO_2 emissions during catalyst activation should remain below the permissible concentrations if the inlet SO_2 is controlled at the appropriate low concentrations relative to the increasing activity of the catalyst. Once completed this procedure is not repeated unless the converter is opened for catalyst cleaning or addition of new catalyst, permitting the adsorption of water vapor.

Cold Plant Start-Up - Dual Absorption

The single absorption acid plant cannot obtain emissions within the permissible limits of the standards in normal operations without the addition of a vent gas cleaning system. The dual absorption acid plant, however, can achieve standard emissions limits. Discussion with plant engineers during plant surveys(8) indicated dual absorption plants can be started from a cold condition without exceeding standard SO_2 emissions. To accomplish a start-up without exceeding standards, the start-up procedure must be performed very carefully maintaining close control on all process parameters. It is also necessary to provide a complete preheat of the converter to obtain maximum conversion efficiency before SO_2 is emitted to the system. Hot concentrated sulfuric acid is required in the drying tower and absorption tower to limit the amount of acid mist generation in the system. Although a clean start-up of a cold plant is possible, it is seldom feasible because of time and production constraints.

This type of start-up is best accomplished in a plant associated with another sulfuric acid plant that can provide hot concentrated acid for charging the air dryer and absorber. Although this type of start-up is ideal and has been demonstrated, a short period of SO_2 emissions exceeding standards is more frequently experienced. Routine difficulties in establishing temperature control around the catalyst beds, will generally cause the emission of SO_2 to exceed the standards for several hours. Difficulties in controlling sulfur feed at a satisfactory rate to control temperatures of the sulfur furnace and concentrations of SO_2 in the converters will also cause SO_2 emissions.

A plant that is not equipped with preheaters must depend upon the reaction of the SO_2 in the converter to heat the converter to final reaction temperatures. With this arrangement high concentrations of SO_2 will be encountered during the rather long period of time required to heat the converter to peak efficiency. This procedure will usually produce emissions in excess of standards for two or more days. A cold start-up procedure for a dual absorption plant is shown in Figure 15, Page 90 of Section VI. Most new sulfuric acid plants being designed today are equipped with adequate preheaters.

Table 12, Page 77 of Section VI summarizes start-up data for plants of all types with various periods of downtime prior to restarting. These figures clearly illustrate the difficulty in obtaining low SO_2 emissions after a shutdown of four hours or more, requiring reheating of the converter.

Warm Plant Start-Ups - Dual Absorption Process

If a plant shutdown has not extended beyond a four hour period and proper heat conservation has been practiced in the plant, catalyst temperatures should be sufficiently high to permit restarting of plant without reheating. In these situations restarting the sulfur flow to the furnace and careful readjustment of dampers to maintain temperatures in the catalyst converter beds will permit restarting the plants without exceeding SO_2 or acid mist standard emissions. The SO_2 emissions during hot start-ups are summarized in Table 12.

Vent Gas Cleaning Systems - Single Absorption

The start-up of vent gas cleaning systems applied to a single absorption acid plant requires very simple operating procedures. The emissions from the vent gas cleaning system will depend largely upon the start-up procedures used in the single absorption plant, since the outlet SO_2 is dependent upon the concentration of SO_2 in the incoming gas to the clean-up system.

Figures 13 and 14, Pages 83 and 88 of Section VII show this relationship with an ammonia scrubbe   As previously stated, the vent gas cleaning systems provide a buffer between the single absorption plant and the vent gas that will reduce the intensity of concentration swings in SO_2 emitted from the single absorption plant. In general terms it appears the sodium and ammonia scrubbing systems can be started up with peak SO_2 emissions one half of those normally encountered in a single absorption plant (Figure 13, Page 83 of Section VI).

Start-up of the ammonia and sodium scrubbing systems requires only the establishment of proper sodium or ammonium concentrations and liquid flow rates through the scrubbers and appropriate pH of the circulating solutions. These conditions are established before starting the sulfur flow to the furnace. The primary operating precautions required to prevent excessive SO_2 emissions from the scrubbers are careful control of temperature, the pH, and concentration of the circulating solutions during the period of increase in SO_2 concentrations from the single absorption plant absorber. Emissions from an ammonia scrubber system during typical start-up are shown in Figure 14 of Section VI.

In an ammonia scrubber system, opacity is most likely to occur in excess of standards during start-up. The quantity of the ammonium sulfite particulate generated in an ammonia scrubber of the types now in use is very sensitive to control of pH and relative concentrations of NH_3 and SO_2. It is possible that the equipment installed to remove this particulate will be overloaded by the excessive amounts of particulate formed during the upset condition experienced during the start-up. In some situations sufficient steam is not available from waste heat boilers during start-up to operate both the air blower and the booster blower required to overcome the pressure drop in the ammonia scrubber particulate filter. In this situation it is routine practice to bypass the particulate filter so the steam driven booster blower is not required. When the filter is bypassed large quantities of particulate matter are emitted from the ammonia scrubber causing a heavy blue plume far in excess of the opacity standards. These emissions can largely be eliminated if arrangements are made to place the particulate filter in operation before SO_2 is introduced to the system.

No data were available on start-up conditions for the Union Carbide molecular sieve system, but according to literature previously published(9) this system is very tolerant to large surges in SO_2 and acid mist concentrations from the absorber and should emit very low levels of these pollutants during a normal start-up of the single absorption plant equipped with the PuraSiv system.

SECTION VIII

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SECTION IX

GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

The following listing is a glossary of terms and abbreviations that are used in this report. Also included is a list of chemical symbols that are found in the report.

GLOSSARY OF TERMS

Absorber

A device utilized to extract selectively one or more elements of a gas stream from others by absorption in a liquid medium. Usually the process is performed in cylindrical towers packed with an inert material thus providing a large surface area for intimate contact between the rising gas and the falling liquid. (The process may also be carried out in a tower containing perforated trays in which the rising gas bubbles through the layer of liquid on the trays.)

Absorption

A process in which one or more constituents are removed from a gas stream by dissolving them in a selective liquid solvent. This may or may not involve a chemical change.

Acid, New

Sulfuric acid made from elemental sulfur or other sulfur-bearing materials, but not from spent acid strengthened by addition of sulfur trioxide.

Acid, Regenerated

High-purity sulfuric acid made from decomposition or regeneration of spent acid from petroleum refineries or other chemical processes.

Acid Sludge

The residue left after treating petroleum oil with sulfuric acid for the removal of impurities. It is a black, viscous substance containing the spent acid and impurities which have been separated from the oil.

Adsorption

A reaction in which one or more constituents (adsorbates) are removed from a gas stream by contacting and adhering to the surface of a solid (adsorbent). Periodically the adsorbent must be regenerated to remove the adsorbate.

Aerosol

A colloidal system in which particles of solid or liquid are suspended in a gas. There is no clear-cut upper limit to the particle size of the dispersed phase in an aerosol, but as in all other collodial systems, it is commonly set at 1 micro-meter. Haze, most smoke, and some fogs and clouds may be regarded as aerosols.

Agglomeration

Groups of fine particles clinging together to form a larger particle.

Ambient Air

That portion of the atmosphere, external to buildings, to which the general public has access.

Boiler

A closed pressure vessel in which the liquid, usually water, is vaporized by the application of heat.

British Thermal Unit (Btu)

The mean British thermal unit is 1/180 of the heat required to raise the temperature of one pound of water from 32°F to 212°F at a constant atmospheric pressure. It is about equal to the quantity of heat required to raise one pound of water 1°F. A Btu is essentially 252 calories.

Burner

A device for the introduction of fuel and air into a furnace at the desired velocities, turbulence, and concentration to establish and maintain proper ignition and combustion of the fuel.

Carryover

The chemical solids and liquid entrained in the steam from a boiler or effluent from a fractionating column, absorber, or reaction vessel.

Catalyst

A substance capable of changing the rate of a reaction without itself undergoing any net change.

The catalyst in a chamber plant is gaseous nitrogen oxides. In the contact process the catalyst is a solid, consisting of vanadium pentoxide and various promotors deposited on a highly porous siliceous carrier.

Claus Elemental Sulfur Plant

A process for converting SO_2 to elemental sulfur by catalytic reaction with H_2S.

Condensed Fumes

Minute solid particles generated by the condensation of vapors from solid matter after volatilization from the molten state, or generated by sublimation, distillation, calcination, or chemical reaction when these processes create airborne particles.

Converter

The vessel that houses the solid vanadium catalyst. The catalyst is placed in several horizontal trays or stages located in series, with means for gas cooling between the various stages.

Demister (Collector)

1. A mechanical device used to eliminate finely divided liquid particles from process streams by impaction and agglomeration.

2. Apparatus made of wire mesh or glass fiber and used to eliminate acid mist as in the manufacture of sulfuric acid.

Economizer

A heat recovery device designed to transfer heat from the products of combustion to a fluid, usually feedwater for a steam boiler. The water flows through a bank of tubes placed across the flue gases and is heated by these gases prior to entering the boiler.

Effluent

Any waste material (solid, liquid, gas) emitted by a process.

Emission

The total amount of a solid, liquid, or gaseous pollutant emitted into the atmosphere from a given source in a given time, and indicated in grams per cubic meter of gas, pounds per hour, or other quantitative measurement.

Entrainment

The process of particulates or other materials being carried along by a gas stream.

Excess Air

Air supplied for combustion in excess of that theoretically required for complete combustion, usually expresses as a percentage of theoretical air, such as "130 percent excess air."

Exothermic Reaction

A reaction which produces heat.

Feedstock

Starting material used in a process. This may be raw material or an intermediate product that will undergo additional processing.

Flue

Any duct, passage, or conduit through which the products of combustion are carried to a stack or chimney (see also Breeching).

Flue Gas

The gaseous products of combustion passing from the furnace into the stack.

Fuel

Any form of combustible matter--solid, liquid, vapor, or gas, excluding combustible refuse.

Fume

Fine solid particles predominately less than 1 micro-meter in diameter suspended in a gas. Usually formed from high-temperature votilization of metals, or by chemical reaction.

Impingement

In air sampling, impingement refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface. 1. Dry impingement: the process of impingement in the gas stream where particulate matter is retained upon the surface against which the stream is directed. The collecting surface may be treated with a film of adhesive. 2. Wet impingement: the process of impingement in a liquid which retains the particulate matter.

Impingement Separators

Devices using the principle that when a gas stream carrying particulate matter impinges on a body, the gas is deflected around the body, while the particles, because of their greater inertia, tend to strike the body and be collected on its surface. The bodies may be in the form of plates, cylinders, ribbons, or spheres.

Material Balance

An accounting of the weights of material entering and leaving a process.

Mesh

The number of holes per linear unit in a sieve or gauze, or the space between the wires of the sieve expressed in inches or millimeters.

Metric Ton

2204.6 pounds or 1000 kilograms.

Mist

A suspension of any finely divided liquid in a gas.

Mist, Sulfuric Acid

Extremely small acid particles that are true aerosols. No exact range of particle size is available.

Net Ton

2000 pounds (sometimes known as a "short ton").

Nitrogen Oxides

A general term pertaining to a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2).

Oleum (Fuming Sulfuric Acid)

A heavy, oily, strongly corrosive liquid that consists of a solution of sulfur trioxide in anhydrous sulfuric acid. It fumes in moist air and reacts violently with water.

Onstream Time

The length of time a unit is in actual production.

Opacity

The degree to which emissions reduce the transmission of light and obscure the view of a distant object.

Orsat

An apparatus used for analyzing flue gases volumetrically.

Oxidation

The act or process of combining oxygen with a substance, with or without the production of a flame.

Oxides, Sulfur

As used in this report, sulfur oxides include sulfur dioxide and sulfur trioxide, and/or sulfuric acid mist or spray.

Packed Column (Packed Scrubber or Packed Tower)

A vertical column used for distillation, absorption, and extraction, containing packing; e.g., Raschig rings, Berl saddles, or crushed rock, which provide a large contacting surface area between phases. Normally, gas flow is countercurrent to liquid flow.

Particulate Matter

Any dispersed matter, solid or liquid, in which the individual aggregates are larger than single small molecules (0.0002 micro-meters) but smaller than 500 micro-meters.

Performance Test

Measurements of emissions used for the purpose of determining compliance with a standard of performance.

Plume

The path taken by the continuous discharges of products from a chimney or stack. The shape of the path and the concentration distribution of gas plumes is dependent on turbulence of the atmosphere.

Primary Air

In incineration, air which is introduced with the refuse into the primary chamber.

Primary Standard

The national primary ambient air quality standard which defines levels of air quality which are necessary to protect public health.

Ringelmann Chart

A standardized chart giving shades of gray by which the densities of columns of smoke rising from stack may be compared.

Scrubber

A device used to remove entrained liquids and solids from a gas stream by passing the gas through wetted "packing" or spray (see absorber).

Secondary Air

Air introduced into a combustion chamber beyond the point of fuel and primary air introduction for the purpose of achieving more complete oxidation.

Smelting

Any metallurgical operation in which metal is separated by fusion from impurities with which it may be chemically combined or physically mixed, such as in ores.

SO_2 Gas or SO_3 Gas

A gas in which SO_2 or SO_3 is present with other constituents such as oxygen or nitrogen.

Spray, Sulfuric Acid

Large acid particles introduced into the gas by mechanical entrainment. If emitted to atmosphere, they are invisible and fall rapidly to the ground.

Stack or Chimney

Any flue, conduit, or duct arranged to conduct an effluent to the open air.

Sulfur, Crude

A low-sulfur-content raw material consisting of a mixture of elemental sulfur and inert material.

Sulfur, Elemental

Any sulfur in elemental form, regardless of source.

Sulfur, Recovered

An extremely high-purity sulfur containing no organic matter, less than 0.005 percent ash, and no free acid or water unless exposed to the atmosphere. (If shipped molten, it may also contain traces of hydrogen sulfide.)

Surge Tank

A storage reservoir at the downstream end of a feeder pipe to absorb sudden rises of pressure and to furnish liquid quickly during a drop in pressure.

Tail Gas

The exhaust or waste gas from a process.

Vapor

The gaseous phase of a substance that generally exists as a liquid or solid at room temperature.

Vapor Plume

The stack effluent consisting of flue gas made visible by condensed water droplets or mist.

Venturi Scrubber

A type of high energy scrubber in which the waste gases pass through a tapered restriction (venturi) and impact with low-pressure water. Gas velocities at the restriction are from 15,000 to 20,000 fpm and pressure drops from 10 to 70 inches water gage.

Visible Emission

An emission of air pollutants greater than 5 percent opacity of 1/4 Ringelmann.

Waste Heat Boilers

Boilers which utilize the heat of exhaust gas or process gas to generate steam or to heat water.

ABBREVIATIONS

°C	temperature, degrees Celsius
ft	feet
ft^2	square feet
ft^3, cf	cubic feet
°F	temperature, degree Fahrenheit
lbs	pounds
Mscfm	thousands of standard cubic feet per minute
ppm	parts per million by volume
psig	pounds per square inch gauge
PSIA	pounds per square inch absolute
scfm	cubic feet per minute measured at standard conditions: (70°F and 760 mm (29.92") Hg
SCFH	standard cubic feet per hour
sp. gr.	specific gravity--compared to water at 60°F

CHEMICAL SYMBOLS

CO_2	carbon dioxide
H_2O	water
NH_3	ammonia
N_2	nitrogen
NO_x	total nitrogen oxides in a mixture
O_2	oxygen
S	sulfur
SO_2	sulfur dioxide
SO_3	Sulfur trioxide
H_2SO_4	sulfuric acid
Na_2SO_3	sodium sulfite
$NaHSO_3$	sodium bisulfite
Na_2SO_4	sodium sulfate
$(NH_4)_2SO_4$	ammonium sulfate
NH_4HSO_3	ammonium bisulfite
$(NH_4)_2SO_3$	ammonium sulfite

UNITS OF MEASURE

Conversion Table

Degrees Fahrenheit (°F) = 9/5 Degrees Celsius (°C) + 32

Inches (in) = 215 Centimeters (cm)

Feet (ft) = 30 Centermeters (cm)

Square Inches (in^2) = 6.5 Square Centimeters (cm^2)

Cubic Feet (ft^3)(cf) = .03 Cubic Meters (m^3)

Pounds (lb) = .45 Kilograms (kg)

Ton (short) = .9 Tonnes (t)

Gallons (gal) = 3.8 Liters (l)

Pounds Per Square Inch (psi) = .06 Kilograms Per Square Centimeter (kg/cm^2)

APPENDIX A

PROCESS DESCRIPTIONS
SULFURIC ACID PRODUCTION
AND
TAIL GAS CLEANING PROCESSES

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TABLE 17

OPERATING DATA FOR THE SULFURIC ACID PLANT (THEORETICAL)

Location in acid plant	Pressure, in. H_2O		Temperature, °C	
	316 tons/day	150 tons/day	316 tons/day	150 tons/day
Enter blower	-5 3/4	-1	0-(32°F)	14-57°F
Enter dry tower	95 1/2	28 1/2	29.0-(85)	
Leave dry tower		--	60-(85)	--
Enter sulfur burner	89 1/2	26 1/2		
Leave sulfur burner	84 1/4	25 3/4	972-(1782)	948-(1738)
Leave boiler #1	78	24 3/4	424-(795)	293-(559)
Enter filter	76	24 1/4	434-(813)	427-(801)
Leave filter	67 3/4	22 1/4	-- --	--
Enter pass #1	66 3/4	22	426-(799)	405-(761)
	60 3/4	19 3/4	476-(889)	476-(889)
Leave pass #1	60 1/4	17 3/4	-- --	-- --
	56 1/4		612-(1134)	603-(1117)
Air enter pass #2	46 1/2	15 3/4	450-(842)	440-(824)
Leave pass #2	37 1/4	12 1/4	510-(750)	491-(916)
Air enter pass #3	26 1/4	12	439-(822)	434-(813)
Leave pass #3	29	9 3/4	447-(837)	439-(822)
Enter pass #4	28 1/4	9 1/2	422-(792)	401-(754)
Leave pass #4	19 3/4	4	426-(799)	400-(152)
Enter economizer	16 3/4	3 1/4	-- --	--
Leave economizer	7	1 1/4	259-(498)	198-(388)
Enter 98 absorber	6 1/2	--	240-(464)	--
Leave 98 absorber	4 3/4	1/2	--	--
Pressure drop (knock out)	1	--	--	--
Pressure drop demister	3 3/8	--	--	--
Leave burner			971-(1780)	948-(1738)
Leave boiler			423-(793)	294-(561)
Enter hot gas filter			434-(813)	430-(806)
Enter "A" layer #1			425-(797)	405-(761)*
Leave "A" layer #1			476-(889)	476-(889)*

*See Table 5

TABLE 17 (Continued)

Location in acid plant	Pressure, in. H_2O 316 tons/day	Pressure, in. H_2O 150 tons/day	Temperature, °C 316 tons/day	Temperature, °C 150 tons/day
Leave "B" layer #1			612-(1134)	603-(1117)*
Enter layer #2			438-(820)	440-(825)
Leave layer #2			500-(932)	491-(916)
Enter layer #3			439-(822)	434-(813)
Leave layer #3			448-(838)	439-(822)
Enter layer #4			423-(793)	401-(754)
Leave layer #4			427-(801)	400-(752)
Leave economizer gas			259-(498)	198-(388)

*See Table 5.

Parameter	316 tons/day	150 tons/day
Blower rpm	4225	2400
% SO_2 after boiler #1	10.3	10.3
% SO_2 into reactor	9.5	8.5
% SO_2 out stack	0.25	0.19
% Conversion	97.55	98.0
Stack appearance	good	good
Boiler #1 bypass valve	28° open	32° open
Boiler #2 bypass valve	closed	3/4 open
Superheater #1 valve	full open	full open
Superheater #2 valve	1/2 open	1/2 open
Saturated steam bypass	closed	closed
Sulfur consumption	212,550 lb/day	
Production rate @ 100% H_2SO_4	632,250 lb/day	2 lb/hr

TABLE 17 (Continued)

Parameter	316 tons/day	150 tons/day
Temperature of sulfur in pit, °C	140°-(284)	140°-(284)
Temperature of sulfur entering burner, °C	140°-(284)	133°-(271)
Saturated steam, psig	338	325
Superheated steam, psig	322	319
Superheated steam, °C	307°-(585)	315°-(599)
110 psig steam to plant, °C	254°-(489)	285°-(545)
Rate of flow to plant, lbs/hr	31,800	15,400
Feed water entering economizer	105°-(221)	104°-(219)
Feed water leaving economizer	208°-(406)	213°-(415)
Temperature of acid entering acid absorber, °C	82-(180)	80-(116)
Temperature of acid leaving acid absorber, °C	120-(248)	91-(198)
Strength leaving acid absorber	99.17%	99.1%
Acid level tank-o-meter, in.	8 1/4	8.2
Temperature of acid entering dry tower, °C	68-(154)	60-(140)
Temperature of acid leaving dry tower, °C	66-(151)	--
Acid level tank-o-meter, in.	7-(45)	7-(75)
Temperature of acid leaving pumps, °C (66°Be')	110-(230°F)	98-(208)

PART 1

SINGLE ABSORPTION PROCESS
FOR
SULFURIC ACID PRODUCTION

MAJOR EQUIPMENT LIST

Figure A-201

SINGLE ABSORPTION SULFURIC ACID PLANT

Equipment Number	Description
K-101	Sulfuric Furnace
F-102	Air Filter
C-103	Main Air Blower
V-104	Drying Tower
B-105	Waste Heat Boiler No. 1
X-106	Economizer After Fourth Bed
V-108	Converter with Four Catalyst Beds
V-109	Secondary Absorber Tower
V-110	Secondary Absorber Acid Cooler
B-111	Waste Heat Boiler No. 2
V-112	Secondary Absorber Acid Pump and Tank
X-113	Product and Storage Tank
X-114	Product Acid Cooler
X-115	Drying Tower Acid Cooler
X-119	Product Acid Cooler

Figure A-201

MATERIAL BALANCE SINGLE ABSORPTION PLANT

Stream No. Description*	(1) Sulfur Feed	(2) Air to Drying Tower	(3) Air to Sulfur Burner	(4) Gas Leaving Sulfur Burner	(5) Gas Entering Converter
Sulfur, S	0.331				
Sulfur Dioxide, SO_2				0.663	0.663
Sulfur Trioxide, SO_3					
Air		2.988	2.988	2.656	2.656
Sulfuric Acid, H_2SO_4					
Sulfuric Acid Mist					
Water		0.030			
Total (tons per day)	0.331	3.018	2.988	3.319	3.319
Temp (°C)	135	50	50	850	410
Pressure (inches water)		85	80	75	60
Composition				10.20 SO_2 (Volume)	
Conversion					
Total (SCFM)		51.9	51.4	50.9	50.9
Total (gal/min)					

*Flow Basis: One ton per day 100 percent H_2SO_4 production.

(Continued)

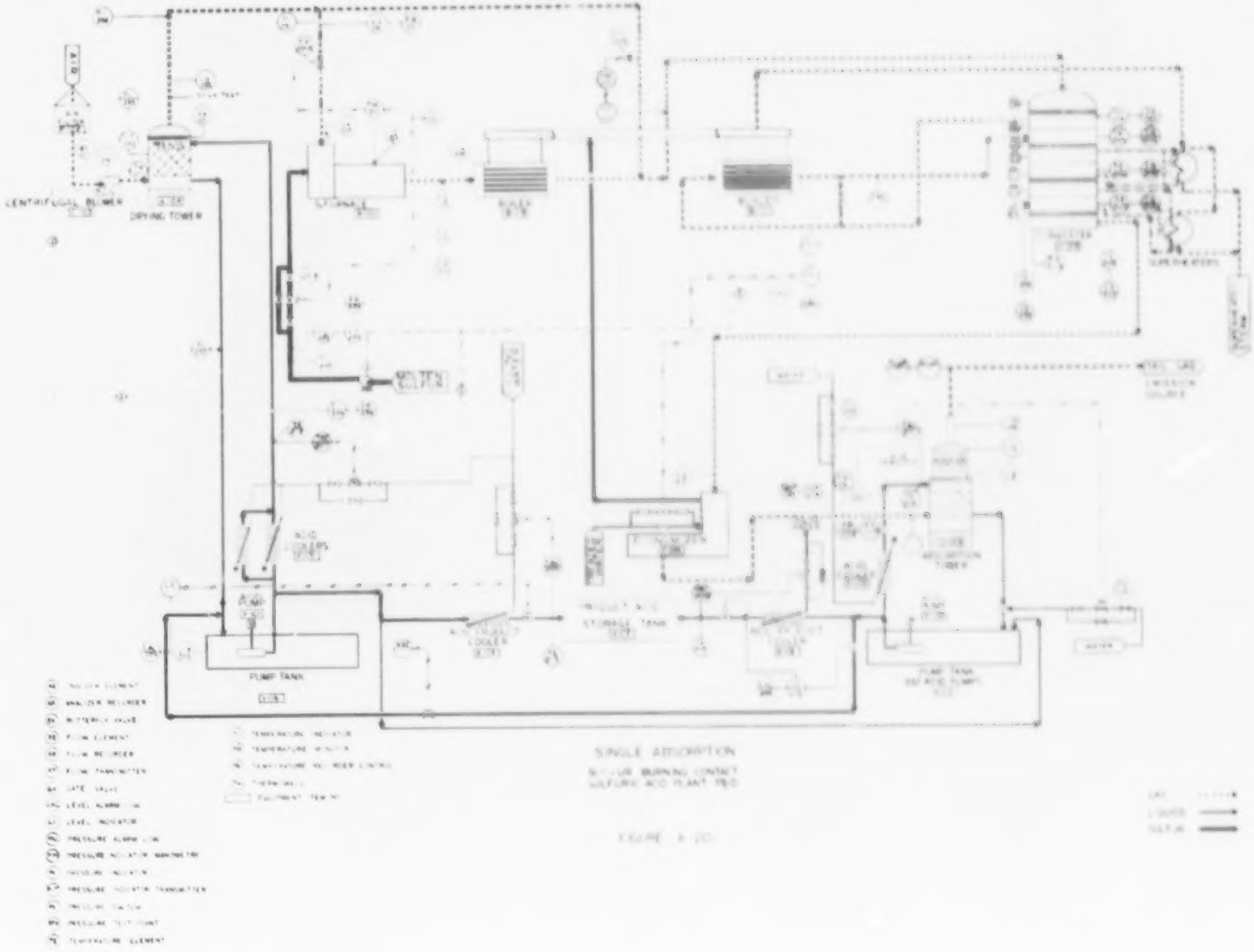
Stream No. Description*	(6) Gas Leaving Converter	(7) Gas Entering Oleum Tower	(8) Oleum Product Leaving Oleum Tower	(9) Gas Leaving Oleum Tower	(10) Gas Entering Absorption Tower (No Oleum Production)
Sulfur, S					
Sulfur Dioxide, SO_2	0.010				0.010
Sulfur Trioxide, SO_3	0.816				0.816
Air	2.493				2.493
Sulfuric Acid, H_2SO_4					
Sulfuric Acid Mist					
Water					
Total (tons per day)	3.319				3.319
Temp. (°C)	445	150	Depends on SO_3 absorbed	75	150
Pressure (inches water)	20	10		3	10
Composition	10.6 SO_3 (Volume)		75% Oleum		
Conversion	98.5% of SO_2 to SO_3				
Total (SCFM)	48.0	48.0			48.0
Total (gal/min)					

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(11) Acid Product	(12) Gas Leaving Absorption Tower	(13) Water for H_2SO_4 Absorption for Absorption Tower	(14) H_2SO_4 for Oleum Tower	(15) H_2SO_4 Circulation to Absorption Tower	(16) H_2SO_4 Circulation to Drying Tower
Sulfur, S						
Sulfur Dioxide, SO_2		.010				
Sulfur Trioxide, SO_3						
Air		2.493				
Sulfuric Acid, H_2SO_4	1.000				10.000	9.098
Sulfuric Acid Mist						
Water	.020	2.503	.183		.200	
Total (tons per day)	1.020		.183		10.200	9.054
Temp. (°C)	70	75	25	70	70	50
Pressure (inches water)		3				
Composition		3995 ppm SO_2				
Conversion						
Total (SCFM)		43.04				
Total (gal/min)	.091		.031		.994	.822

*Flow Basis: One ton per day 100% H_2SO_4 production.


AIR
CENTRIFUGAL BLOWER
DRYING TOWER
STORAGE
MOLTEN SULFUR
BOILER
BOILER
CONVERTER
SUPERHEATERS
ACID COOLERS
PUMP TANK
PRODUCT ACID STORAGE TANK
ACID PRODUCT COOLER
ABSORPTION TOWER
PUMP TANK 98% ACID PUMPS
WATER
STACK GAS EMISSION SOURCE
ANALYZER ELEMENT
ANALYZER RECORDER
BUTTERFLY VALVE
FLOW ELEMENT
FLOW RECORDER
FLOW TRANSMITTER
GATE VALVE
LEVEL ALARM LOW
LEVEL INDICATOR
PRESSURE ALARM LOW
PRESSURE INDICATOR MANOMETER
PRESSURE INDICATOR
PRESSURE INDICATOR TRANSMITTER
PRESSURE SWITCH
PRESSURE TEST POINT
TEMPERATURE ELEMENT
TEMPERATURE INDICATOR
TEMPERATURE MONITOR
TEMPERATURE RECORDER CONTROL
THERMOWELL
EQUIPMENT TAG NO.
GAS
LIQUID
SULFUR

SINGLE ABSORPTION

SULFUR BURNING CONTACT SULFURIC ACID PLANT P&ID

FIGURE 4-20

167

PART 2

DUAL ABSORPTION PROCESS
FOR
SULFURIC ACID PRODUCTION

MAJOR EQUIPMENT LIST

Figure A-202

DUAL ABSORPTION SULFURIC ACID PLANT

Equipment Number	Description
K-201	Sulfur Furnace
F-202	Air Filter
C-203	Main Air Blower
V-204	Drying Tower
B-205	Waste Heat Boiler
X-206	Economizer After Fourth Bed
X-207	Economizer After Third Bed
V-205	Converter With Four Catalyst Beds
V-209	Secondary Absorption Tower
X-210	Secondary Absorber Acid Cooler
X-211	No. 1 Heat Exchanger
V-212	Primary Absorber Acid Pump and Tank
V-213	Product Acid Storage Tank
X-214	Product Acid Cooler
X-215	Drying Tower Acid Cooler
V-216	Drying Tower and Secondary Absorber Acid Pumps
X-217	No. 2 Heat Exchanger
X-218	Steam Superheater
X-219	Product and Cooler
X-220	Primary Absorber Acid Cooler
V-221	Primary Absorber Tower

Figure A-202

MATERIAL BALANCE DUAL ABSORPTION PLANT

Stream No. Description*	(1) Sulfur Feed	(2) Air to Drying Tower	(3) Air to Sulfur Burner	(4) Gas Leaving Sulfur Burner
Sulfur, S	.327			
Sulfur Dioxide, SO_2				.653
Sulfur Trioxide, SO_3				
Air		2.945	2.945	2.618
Sulfuric Acid, H_2SO_4				
Sulfuric Acid Mist				
Water		0.030		
Total (tons per day)	.327	2.945	2.945	3.271
Temp. (°C)	135	50	50	850
Pressure (inches water)		78	76	75
Composition				10.1 SO_2 (Volume)
Conversion				
Total (SCFM)		51.2	51.2	50.2
Total (gal/min)				

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(5) Gas Entering Converter	(6) Gas Leaving 3rd Stage of Converter	(7) Gas Entering Oleum Tower	(8) Oleum Product Leaving Oleum Tower
Sulfur, S				
Sulfur Dioxide, SO_2	.653	.021		
Sulfur Trioxide, SO_3		.790		
Air	2.618	2.460		
Sulfuric Acid, H_2SO_4				
Sulfuric Acid Mist				
Water				
Total (tons per day)	3.271	3.271		
Temp. (°C)	410	445	150	Depends on SO_2 absorbed
Pressure (inches water)	70	55	44	
Composition		10.4% SO_3 (Volume)		25% Oleum
Conversion		96.7% Conversion of SO_2 to SO_3		
Total (SCFM)	50.2	47.4		
Total (gal/min)				

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(9) Gas Leaving Oleum Tower	(10) Gas Entering Primary Absorption Tower (No Oleum Production)	(11) Acid Product	(12) Gas Leaving Primary Absorption Tower
Sulfur, S				
Sulfur Dioxide, SO_2		.021		.021
Sulfur Trioxide, SO_3		.790		
Air		2.460		2.460
Sulfuric Acid, H_2SO_4			1.000	
Sulfuric Acid Mist				
Water				
Total (tons per day)		3.271	1.000	2.481
Temp. (°C)	75	150		75
Pressure (inches water)	40	44		40
Composition				8700 ppm SO_2
Conversion				
Total (SCFM)		47.4		42.5
Total (gal/min)			0.0908	

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

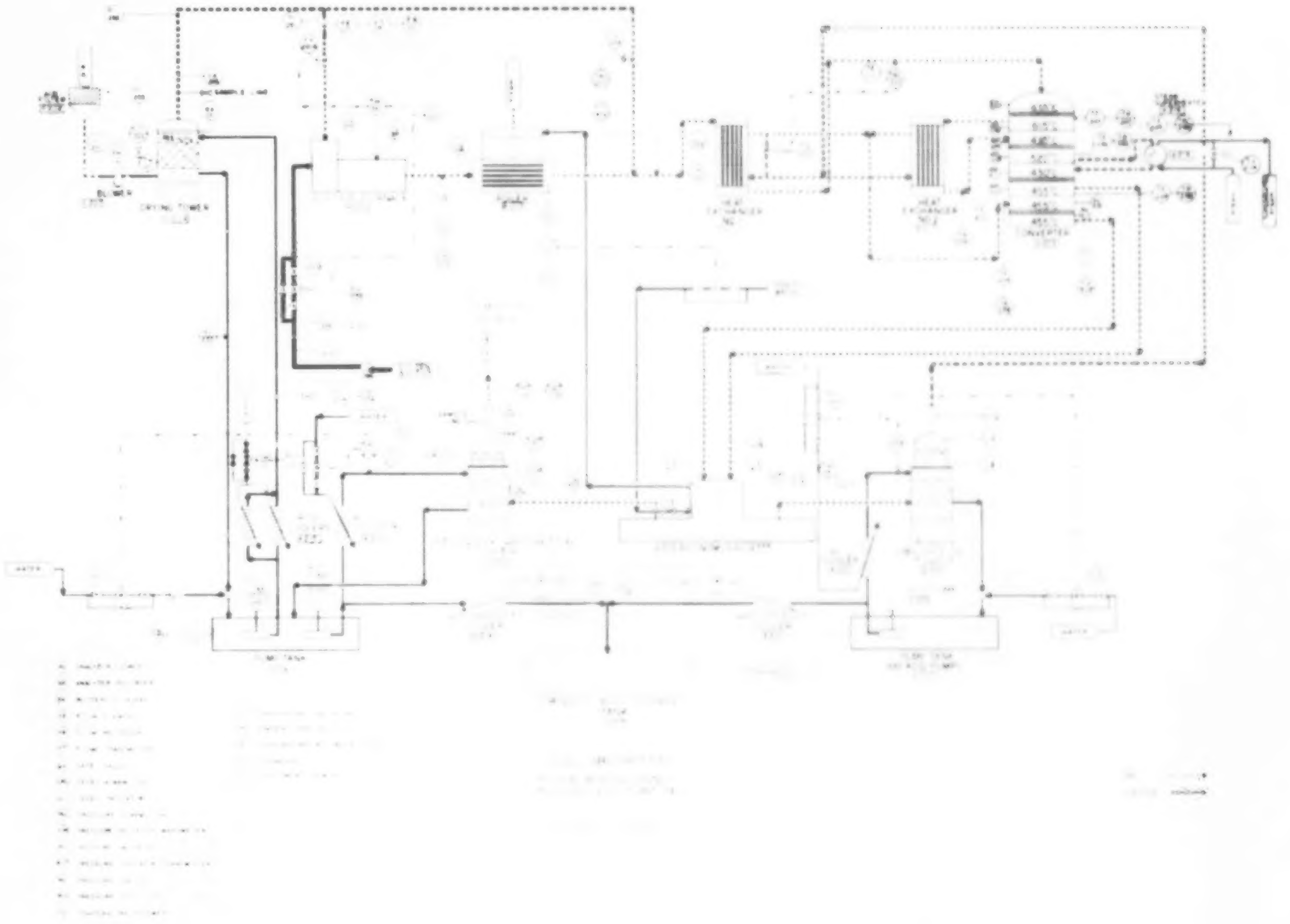
Stream No. Description*	(13) Water for H_2SO_4 Absorption for Absorption Towers	(14) H_2SO_4 for Oleum Tower	(15a) H_2SO_4 Circulation to Primary Absorption Tower	(15b) H_2SO_4 Circulation to Secondary Absorption Tower
Sulfur, S				
Sulfur Dioxide, SO_2				
Sulfur Trioxide, SO_3				
Air				
Sulfuric Acid, H_2SO_4			10.953	8.532
Sulfuric Acid Mist				
Water	.184			
Total (tons per day)	.184		10.953	8.532
Temp. (°C)	25	70	70	70
Pressure (inches water)				
Composition				
Conversion				
Total (SCFM)				
Total (gal/min)	0.030		0.994	0.775

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(16) H_2SO_4 Circulation to Drying Tower	(17) Gas Entering 4th Stage of Converter	(18) Gas Leaving 4th Stage of Converter	(19) Gas Entering Secondary Absorption Tower	(20) Tail Gas from Secondary Absorber
Sulfur, S					
Sulfur Dioxide, SO_2		.021	.0005	.0005	.0005
Sulfur Trioxide, SO_3			.026	.026	
Air		2.460	2.455	2.455	2.455
Sulfuric Acid, H_2SO_4	9.054				
Sulfuric Acid Mist					
Water					
Total (tons per day)	9.054	2.481	2.481	2.481	2.455
Temp. (°C)	50	425	430	150	75
Pressure (inches water)		40	25	15	3
Composition					220 ppm SO_2
Conversion					
Total (SCFM)		42.5	42.4	42.4	42.2
Total (gal/min)	0.822				

*Flow Basis: One ton per day 100% H_2SO_4 production.



BLOWER
DRYING TOWER
HEAT EXCHANGER NO.1
HEAT EXCHANGER NO.2
CONVERTER
PUMP TANK
PUMP TANK

PART 3

SODIUM SCRUBBING PROCESS
FOR
SULFURIC ACID TAIL GAS CLEANING

MAJOR EQUIPMENT LIST

Figure A-203

SODIUM SCRUBBING PROCESS

Equipment Number	Description
B-301	Booster Fan
V-302	Prescrubber
P-303	Prescrubber Circulation Pump
D-304	Demister
V-305	SO_2 Scrubber
D-306	SO_2 Scrubber Demister Pad
P-307	SO_2 Scrubber Circulation Pump
V-308	Brine Holding Tank
A-309	Brine Holding Tank Agitator
P-310	Brine Feed Pump to Evaporator - Crystallizer
V-311	Evaporator - Crystallizer
X-312	Heat Exchanger for Evaporator - Crystallizer
P-313	Evaporator-Crystallizer Recirculation Pump
P-314	Evaporator-Crystallizer Discharge Pump
S-315	Centrifuge
V-316	Mother Liquor Tank
A-317	Mother Liquor Tank Agitator
P-318	Mother Liquor Discharge Pump
C-319	Conveyor for Na_2SO_3 Crystals to Dissolving Tank
V-320	Dissolving Tank

Equipment Number	Description
A-321	Dissolving Tank Agitator
P-322	Dissolving Tank Pump
X-323	Condenser
V-324	Separator Tank
P-325	Separator Tank Condensate Pump
V-326	50 Percent NaOH Storage Tank
P-327	50 Percent NaOH Pump
V-328	Alkali Make-Up Tank
D-329	Alkali Make-Up Tank Discharge Pump

Figure A-203

MATERIAL BALANCE SODIUM SCRUBBING PROCESS

Stream No. Description*	(1) Tail Gas Entering Packed Tower Gas Scrubber	(2) Cleaned Gas Leaving Packed Tower Gas Scrubber	(3) Sodium Hydroxide Make-Up to Packed Gas Scrubber
Sulfur, S			
Sulfur Dioxide, SO_2	0.00994	0.00050	
Sulfur Trioxide, SO_3			
Air			
Sulfuric Acid	2.822	2.822	
Sulfuric Acid Mist			
Water			.001316
Sodium Bisulfite, $NaHSO_3$			
Sodium Sulfite, Na_2SO_3			
Sodium Sulfate, Na_2SO_4			
Sodium Hydroxide, NaOH			.001316
Total (tons per day)	2.83194	2.8225	.002632
Total (SCFM)	51.38	51.30	
Total (Gallons per minute)			.000322
Temp. (°C)	75	75	30
Pressure (inches of water)			
Composition	1560 ppm SO_2	86 ppm SO_2	
Conversion		95% Scrubber Efficiency	

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(4) Scrubber Brine Bleed to Holding Tank	(5) Scrubber Brine Recirculation to Packed Gas Scrubber	(6) Brine Feed from Holding Tank to Evaporator-Crystallizer	(7) Gas Exiting the Evaporator-Crystallizer
Sulfur, S				
Sulfur Dioxide, SO_2				0.00381
Sulfur Trioxide, SO_3				
Air				
Sulfuric Acid				
Sulfuric Acid Mist				
Water	0.3552	5.6054	0.3552	0.03810
Sodium Bisulfite, $NaHSO_3$	0.01238	1.9534	0.01238	
Sodium Sulfite, Na_2SO_3	0.00323	0.5096	0.00323	
Sodium Sulfate, Na_2SO_4	0.00269	0.4246	0.00269	
Sodium Hydroxide, NaOH				
Total (tons per day)	0.05382	8.493	0.05382	0.04191
Total (SCFM)				1.0851
Total (Gallons per minute)	0.00896	1.414	0.00896	1.9851
Temp. (°C)				
Pressure (inches of water)				
Composition				
Conversion				

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

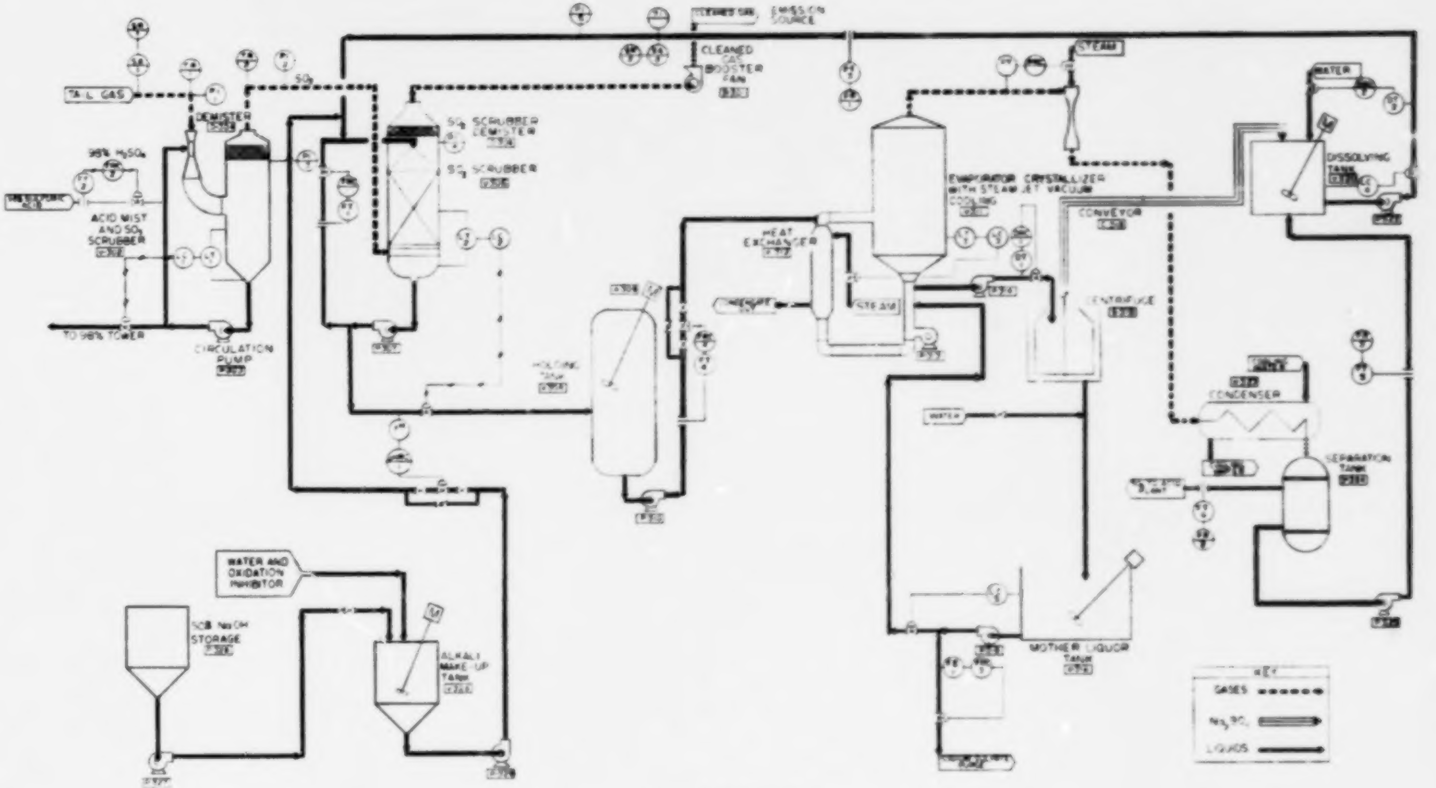
Stream No. Description*	(8) Gas Entering the Separator Tank	(9) SO_2 Recycle Gas to Acid Plant	(10) Condensate from Separator Tank Recycled to Dissolving Tank	(11) Concentrated Liquor Feed to Centrifuge
Sulfur, S				
Sulfur Dioxide, SO_2	0.00381	0.00381		
Sulfur Trioxide, SO_3				
Air				
Sulfuric Acid				
Sulfuric Acid Mist				
Water	0.03810		0.03810	0.00152
Sodium Bisulfite, $NaHSO_3$				
Sodium Sulfite, Na_2SO_3				0.00899
Sodium Sulfate, Na_2SO_4				0.00465
Sodium Hydroxide, NaOH				
Total (tons per day)	0.04191	0.00381	0.03810	0.01516
Total (SCFM)	1.9851	0.02968.		
Total (Gallons per minute)			0.00634	
Temp. (°C)				
Pressure (inches of water)				
Composition				
Conversion				

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(12) Na_2SO_3 Crystals to Dissolving Tanks	(13) Na_2SO_3 Slurry Recycle to Packed Gas Scrubber	(14) Na_2SO_3 and Na_2SO_4 Slurry to Mother Liquor Tank	(15) Na_2SO_3 and Na_2SO_4 Recycle to Evaporator Crystallizer	(16) Na_2SO_4 Purge
Sulfur, S					
Sulfur Dioxide, SO_2					
Sulfur Trioxide, SO_3					
Air					
Sulfuric Acid					
Sulfuric Acid Mist					
Water	.000745	.01824	.000775	.000775	.000388
Sodium Bisulfite, $NaHSO_3$					
Sodium Sulfite, Na_2SO_3	.00546	.00546	.00353	.00353	.00177
Sodium Sulfate, Na_2SO_4			0.00465	0.00465	.00233
Sodium Hydroxide, NaOH					
Total (tons per day)	.006205	.0237	.00896	.00896	.00449
Total (SCFM)					
Total (Gallons per minute)					
Temp. (°C)					
Pressure (inches of water)					
Composition					
Conversion					

*Flow Basis: One ton per day 100% H_2SO_4 production.



TAIL GAS
DEMISTER
98% H_2SO_4
ACID MIST AND SO_3 SCRUBBER
TO 98% TOWER
CIRCULATION PUMP
SO_2
SO_2 SCRUBBER DEMISTER
SO_2 SCRUBBER
CLEANED GAS BOOSTER FAN
EMISSION SOURCE
HOLDING TANK
HEAT EXCHANGER
STEAM
EVAPORATOR CRYSTALLIZER WITH STEAM JET VACUUM COOLING
CONVEYOR
CENTRIFUGE
WATER
DISSOLVING TANK
CONDENSER
SEPARATION TANK
MOTHER LIQUOR TANK
WATER AND OXIDATION INHIBITOR
50% NaOH STORAGE
ALKALI MAKE-UP TANK
KEY
GASES
Na_2SO_4
LIQUIDS

SODIUM SCRUBBER

TAIL GAS CLEANING SYSTEM P&ID

FIGURE A-203

PART 4

AMMONIA SCRUBBING PROCESS
FOR
SULFURIC ACID TAIL GAS CLEANING

MAJOR EQUIPMENT LIST

Figure A-204

AMMONIA SCRUBBING PROCESS

Equipment Number	Description
V-400	Packed Tower Gas Scrubber - 1
P-401	Ammonia Scrubber Brine Circulation Pump
V-402	Packed Tower Gas Scrubber - 2
V-503	Ammonia Scrubber Brine Circulation Pump
V-504	I.D. Exhaust Fan
V-405	Holding Tank
V-406	Holding Tank Mixer
V-407	Ammonia Brine Preparation Tank Mixer
F-408	Brink Filter
P-409	Ammonia Brink Preparation Tank Pump
X-410	Ammonia Vaporizer
V-411	Ammonia Brine Preparation Tank

Figure A-204

MATERIAL BALANCE AMMONIA SCRUBBING PROCESS

Stream No. Description*	(1) Tail Gas Entering Packed Tower Gas Scrubbers	(2) Cleaned Gas Leaving Packed Tower Gas Scrubbers	(3) Ammonia Make-Up to Packed Tower Gas Scrubber
Sulfur, S			
Sulfur Dioxide, SO_2	0.00994	0.00050	
Sulfur Trioxide, SO_3			
Air	2.822	2.822	
Sulfuric Acid, H_2SO_4			
Sulfuric Acid Mist			
Water			
Ammonium Bisulfite, NH_4HSO_3			
Ammonium Sulfite, $(NH_4)_2SO_3$			
Ammonium Sulfate, $(NH_4)_2SO_4$			
Ammonia (Anhydrous)			0.00189
Total (tons per day)	2.83194	2.8225	0.00189
Total (SCFM)	51.38	51.30	0.05544
Total (gal/min)			
Temp. (°C)	75	75	25
Pressure (inches water)			
Composition	1560 ppm SO_2	86 ppm SO_2	
Conversion		95% Scrubber Efficiency	

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(4) Scrubber Brine Bleed to Holding Tank	(5a) Scrubber Brine Recirculation	(5b) Scrubber Brine Circulation	(6) Brine Feed to Regeneration Column
Sulfur, S				
Sulfur Dioxide, SO_2				
Sulfur Trioxide, SO_3				
Air				
Sulfuric Acid, H_2SO_4				
Sulfuric Acid Mist				
Water	0.02641	2.633	2.633	0.02641
Ammonium Bisulfite, NH_4HSO_3	0.01039	0.9595	0.9595	0.01039
Ammonium Sulfite, $(NH_4)_2SO_3$	0.00377	0.4035	0.4035	0.00377
Ammonium Sulfate, $(NH_4)_2SO_4$	0.00204	0.2505	0.2505	0.00204
Ammonia (Anhydrous)				
Total (tons per day)	0.04261	4.2465	4.2465	0.04261
Total (SCFM)				
Total (gal/min)	0.00710	0.707	0.707	0.00710
Temp. (°C)				
Pressure (inches water)				
Composition				
Conversion				

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

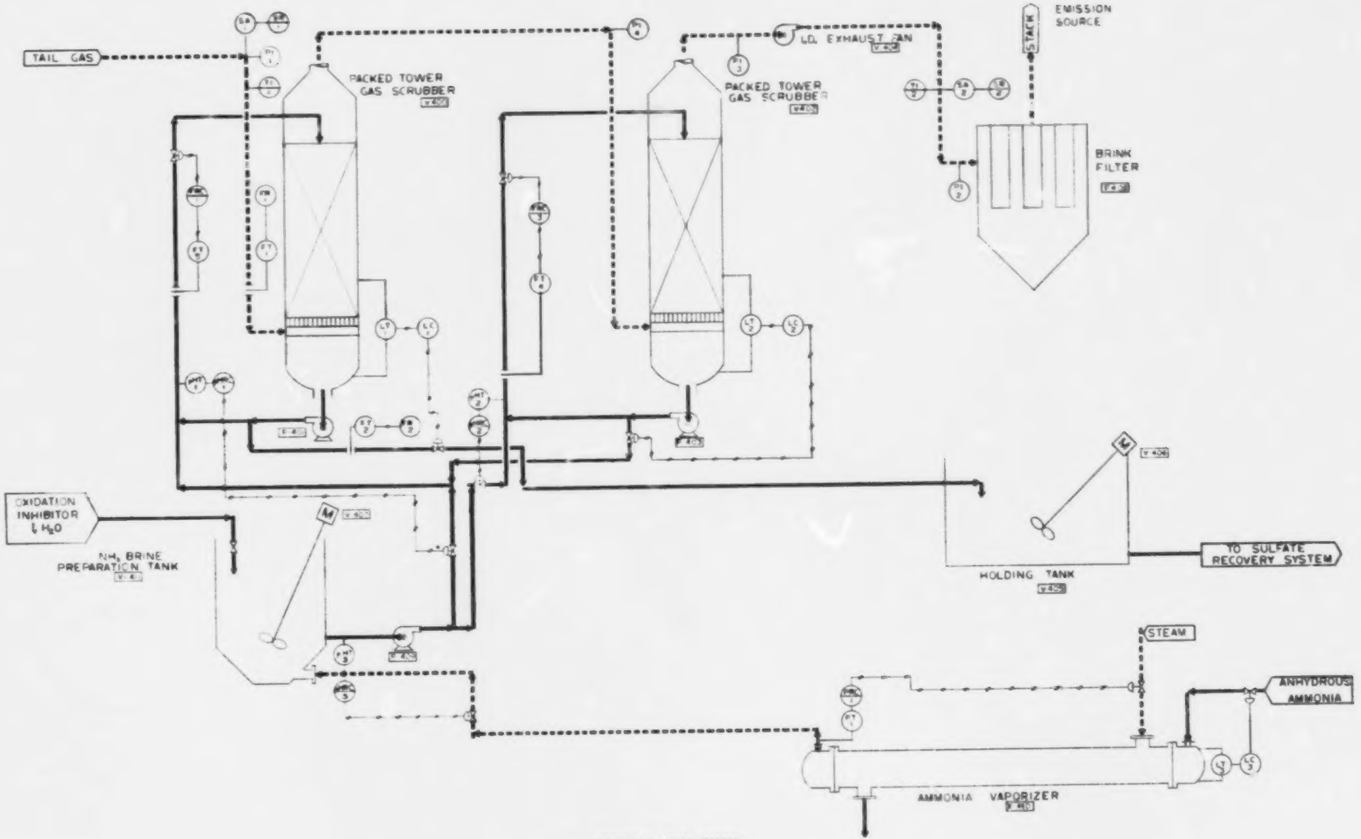
Stream No. Description*	(7) Gas Exiting the Regeneration Column	(8) Gas Entering the Separator Tank	(9) SO_2 Recycle Gas to Acid Plant	(10) Feed to Vertical Tube Evaporator	(11) Ammonium Sulfate Solution Feed to Centrifuge
Sulfur					
Sulfur Dioxide, SO_2	0.003355	0.003355	0.003355		
Sulfur Trioxide, SO_3					
Air					
Sulfuric Acid, H_2SO_4					
Sulfuric Acid Mist					
Water	0.000945	0.000945		0.02641	0.00129
Ammonium Bisulfite, NH_4HSO_3					
Ammonium Sulfite, $(NH_4)_2SO_3$					
Ammonium Sulfate, $(NH_4)_2SO_4$				0.01325	0.01325
Ammonia (Anhydrous)					
Total (tons per day)	0.004300	0.004300	0.003355	0.03966	0.01454
Total (SCFM)	0.0523	0.523	0.0261		
Total (gal/min)					
Temp. (°C)					
Pressure (inches water)					
Composition					
Conversion					

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(12) Ammonium Sulfate Feed to Dryer	(13) Ammonium Sulfate Recycle to Vertical Tube Evaporator	(14) Ammonium Sulfate Exiting the Dryer	(15) Ammonium Sulfate to Storage
Sulfur, S				
Sulfur Dioxide, SO_2				
Sulfur Trioxide, SO_3				
Air				
Sulfuric Acid, H_2SO_4				
Sulfuric Acid Mist				
Water	0.00036	0.00093	0.00003	0.00003
Ammonium Bisulfite, NH_4HSO_3				
Ammonium Sulfite, $(NH_4)_2SO_3$				
Ammonium Sulfate, $(NH_4)_2SO_4$	0.00265	0.01060	0.00265	0.00265
Ammonia (Anhydrous)				
Total (tons per day)	0.00301	0.01153	0.00268	0.00268
Total (SCFM)				
Total (gal/min)				
Temp. (°C)				
Pressure (inches water)				
Composition				
Conversion				

*Flow Basis: One ton per day 100% H_2SO_4 production.


TAIL GAS
PACKED TOWER GAS SCRUBBER
PACKED TOWER GAS SCRUBBER
V 402
I.D. EXHAUST FAN
STACK
EMISSION SOURCE
BRINK FILTER
OXIDATION INHIBITOR & H2O
NH4 BRINE PREPARATION TANK
M
M
V 406
HOLDING TANK
V 405
TO SULFATE RECOVERY SYSTEM
STEAM
ANHYDROUS AMMONIA
AMMONIA VAPORIZER
PI 1
TI 1
LT 1
LC 1
LT 2
LC 2
PI 2
PI 3
PMT 2
PMT 3
FT 2
PT 1
LT 3
LC 3

AMMONIA SCRUBBER
TAIL GAS CLEANING SYSTEM P&ID

FIGURE A-204

PART 5

MOLECULAR SIEVE PROCESS FOR SULFURIC ACID TAIL GAS CLEANING

MAJOR EQUIPMENT LIST

Figure A-205

MOLECULAR SIEVE PROCESS

Equipment Number	Description
X-500	Tail Gases Cooler
X-501	Tail Gases Demister
V-502	Acid Circulation Pot
P-503	Acid Circulation Pot Pump
V-504	SO_2 Absorbers
P-505	I.D. Fan for Tail Gases
F-506	Air Filter
X-507	Condenser
V-508	Air Dryers
X-509	Furnaces
P-510	I.D. Fan for Air
D-511	Drier Regeneration Fan
X-512	SO_2 Gas Cooler

Figure A-205

MATERIAL BALANCE - MOLECULAR SIEVE PROCESS

Stream No. Description*	(1) Tail Gases Entering Demister	(2) Demisted Gases Entering SO_2 Adsorbers	(3) Collected Mist Flow from Demister To Acid Circulation Pot
Sulfur, S			
Sulfur Dioxide	0.00994	0.00994	
Sulfur Trioxide, SO_3			
Sulfuric Acid Mist	0.00082	0.000082	0.000738
Water			
Air	2.822	2.822	
Total (tons per day)	2.833	2.832	
Total (SCFM)	51.38	51.38	
Temperature (°F)	170	170	
Pressure (inches of H_2O)	35 in. H_2O	28 in. H_2O	
Composition	1560 ppm SO_2	1560 ppm SO_2	
Removal Efficiency			90% Acid Mist Removal

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

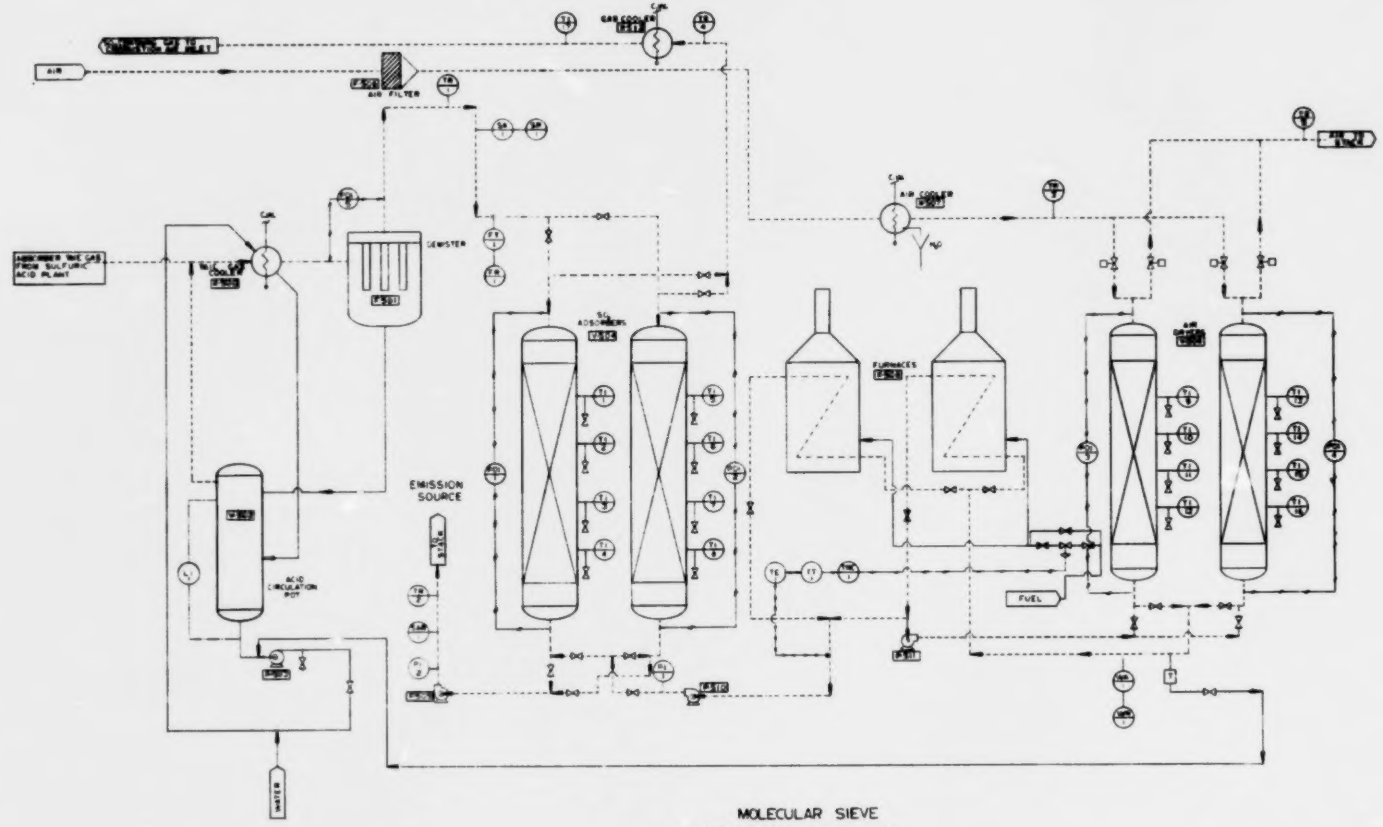
Stream No. Description*	(4) Clean Gases Out from Adsorbers to Stack	(5) SO_2 Containing Desorbed Gases Recycled to Acid Plant	(6) Air Flow to Air Dryers
Sulfur, S			
Sulfur Dioxide, SO_2	0.0000994	0.00994	
Sulfur Trioxide, SO_3			
Sulfuric Acid Mist			
Water			0.0115
Air	2.8220	0.5644	0.5650
Total (tons per day)	2.8221	0.56434	0.5765
Total (SCFM)	51.38	10.5	10.5
Temperature (°F)	100	200	60
Pressure (inches of H_2O)	18 in. H_2O		
Composition	15-25 ppm SO_2	6000 ppm SO_2	
Removal Efficiency	99% SO_2		

*Flow Basis: One ton per day 100% H_2SO_4 production.

(Continued)

Stream No. Description*	(7) Dry Air Flow From Air Dryers To Furnaces	(8) Dry Heated Air Flow From Furnaces To Adsorbers
Sulfur, S		
Sulfur Dioxide, SO_2		
Sulfur Trioxide, SO_3		
Sulfuric Acid Mist		
Water		
Air	0.565	0.565
Total (tons per day)	0.565	0.565
Total (SCFM)	10.5	10.5
Temperature (°F)	60	200
Pressure (inches of H_2O)		
Composition		
Removal Efficiency		

*Flow Basis: One ton per day 100% production.


AIR
AIR FILTER
GAS COOLER
C.W.
ABSORBER TAIL GAS FROM SULFURIC ACID PLANT
TAIL GAS COOLER
C.W.
DEMISTER
ACID CIRCULATION POT
WATER
EMISSION SOURCE
TO STACK
SO2 ADSORBERS
FT
TR
SA
SP
TI
FURNACES
AIR COOLER
C.W.
H2O
AIR DRYERS
TE
FT
FUEL

MOLECULAR SIEVE
TAIL GAS CLEANING SYSTEM P&ID

FIGURE A-205

APPENDIX B

PLANT START-UP DATA

LIST OF FIGURES

Appendix B

No.

25 Dual Absorption Plant Start-Up 8 June 1974 Three Hours to Compliance

26 Dual Absorption Plant Start-Up of 29 June 1973 - A Series of Two Malfunctions With Each Start-Up Requiring Less Than One Hour to Reach EPA Standard

27 Single Absorption Plant Start-Up 20 August 1973 Unstable Start-Up of Less Than Two Hours After Two Hour Shutdown

28 Dual Absorption Plant 6 September 1973 Shutdown

29 Dual Absorption Plant 7 September Shutdown

30 Dual Absorption Plant 11 September 1973 Start-Up

31 Dual Absorption Plant 16 September 1973 Start-Up

32 Single Absorption Plant 17 September 1973 Start-Up

33 Dual Absorption Plant 2 October 1973 Start-Up

34 Dual Absorption Plant 23-24 October 1973 Start-Up

35 Dual Absorption Plant 31 October 1973 Start-Up

36 Dual Absorption Plant 20 November 1973 Start-Up

37 Dual Absorption Plant 27 November 1973 Start-Up

38 Dual Absorption Plant 29 November 1973 Start-Up

39 Dual Absorption Plant 1 December 1973 Start-Up

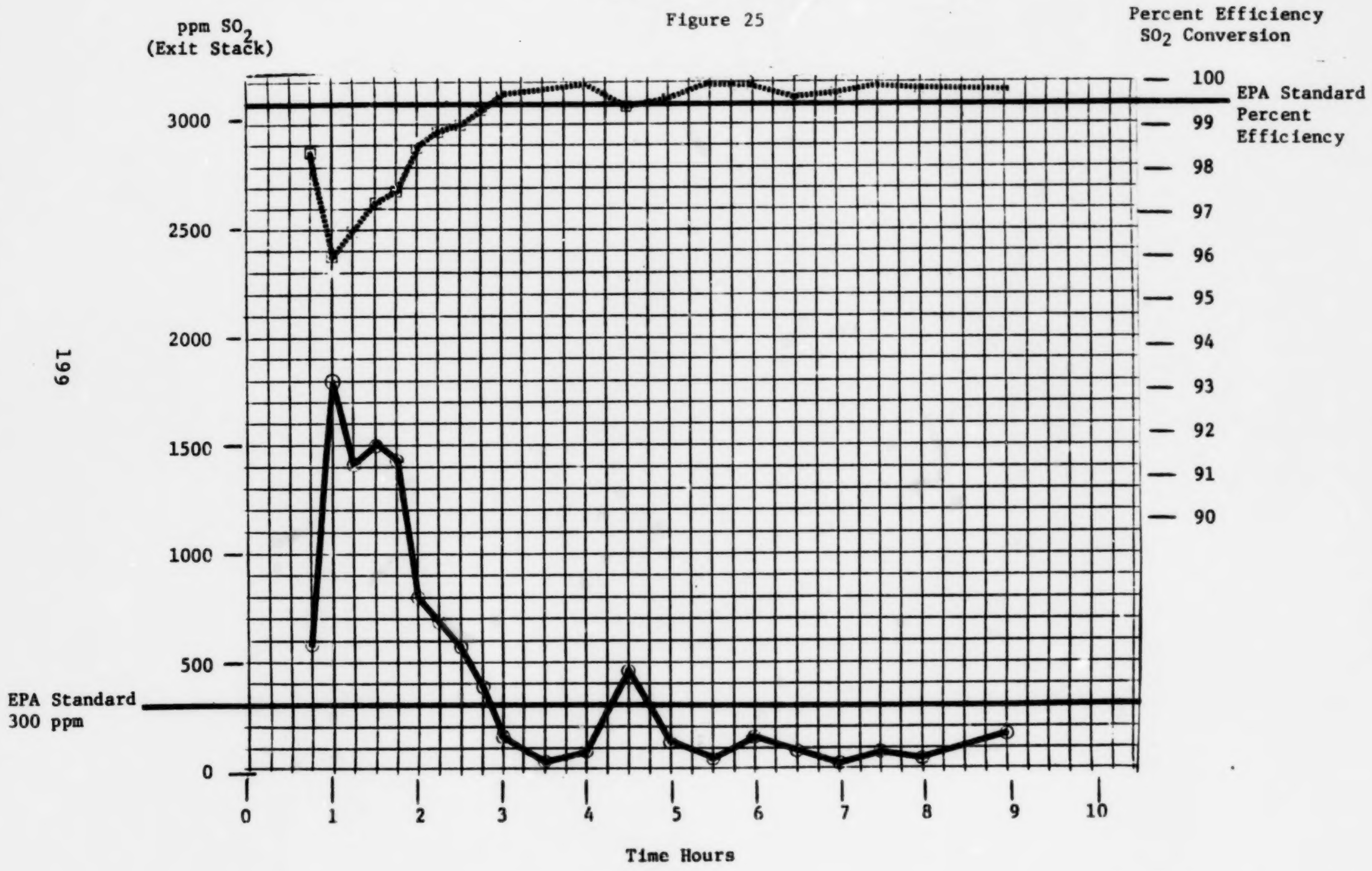
40 Dual Absorption Plant 30 April 1974 Start-Up

41 Dual Absorption Plant 20 October 1974 Start-Up

DUAL ABSORPTION PLANT

START-UP 8 JUNE 1973
3 HOURS TO EPA COMPLIANCE

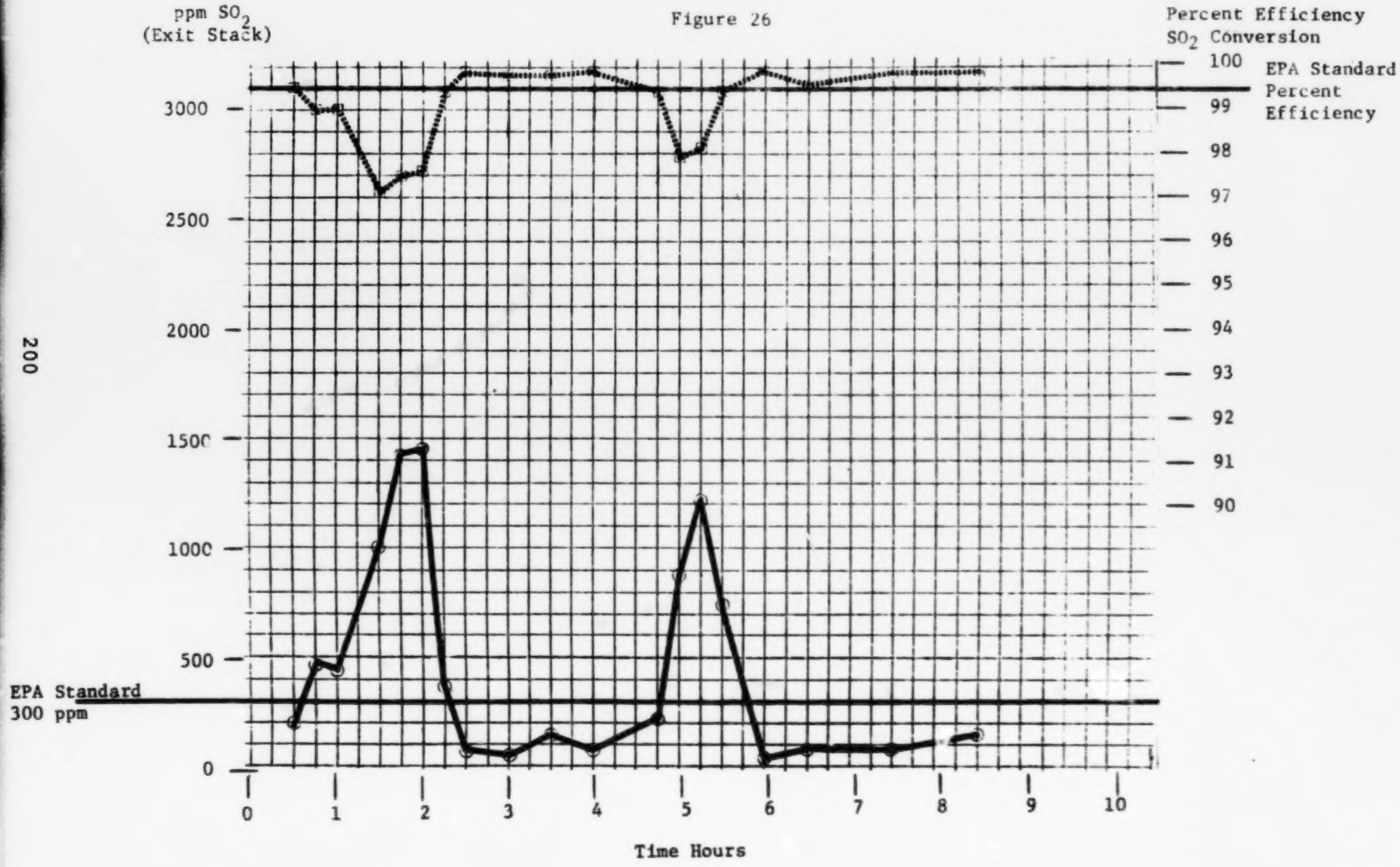
Figure 25



DUAL ABSORPTION PLANT

START-UP OF 29 JUNE 1973 A SERIES OF TWO MALFUNCTIONS WITH EACH START-UP REQUIRING LESS THAN ONE HOUR TO REACH EPA STANDARD

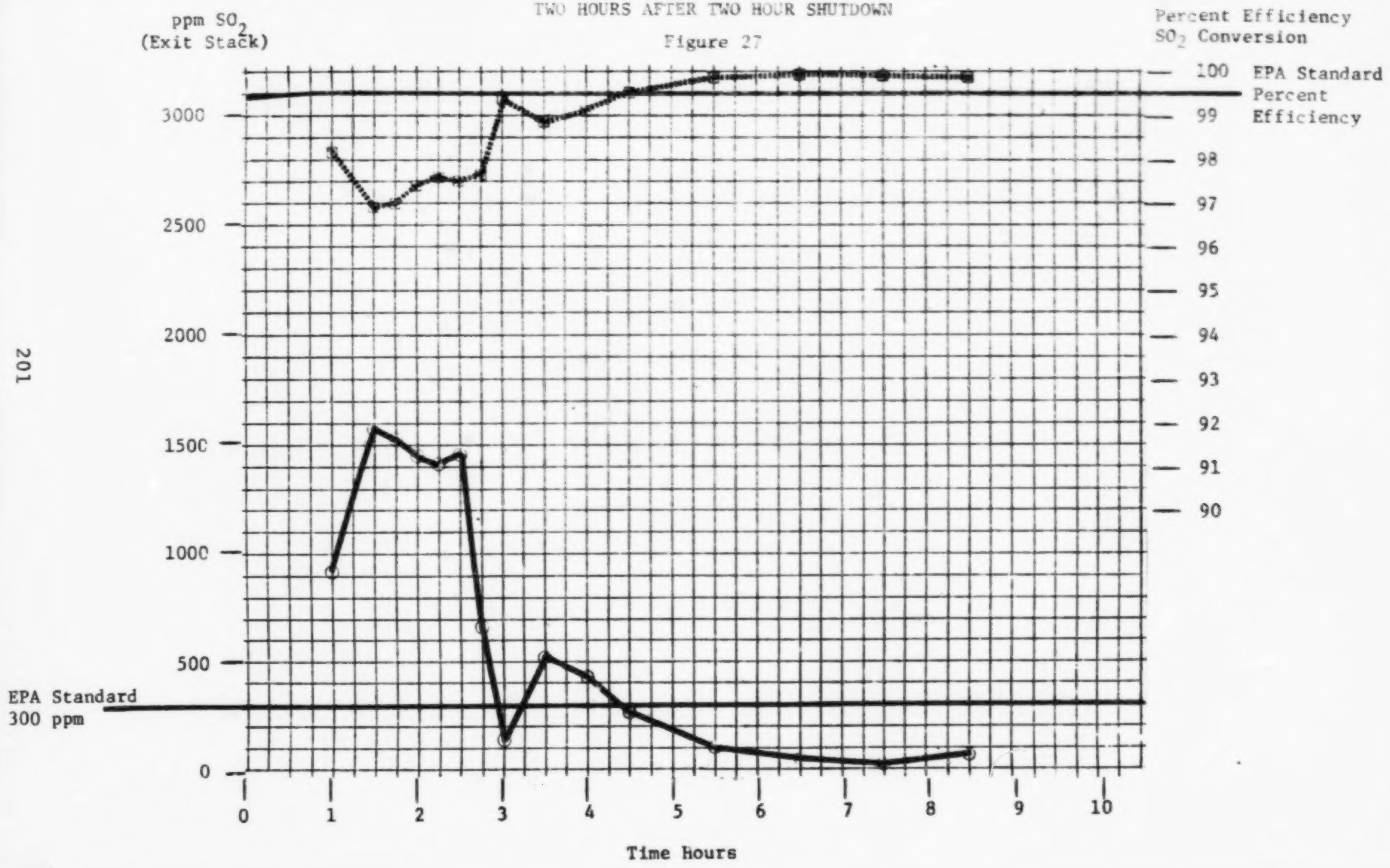
Figure 26



SINGLE ABSORPTION PLANT

START-UP 20 AUGUST 1973
UNSTABLE START-UP OF LESS THAN
TWO HOURS AFTER TWO HOUR SHUTDOWN

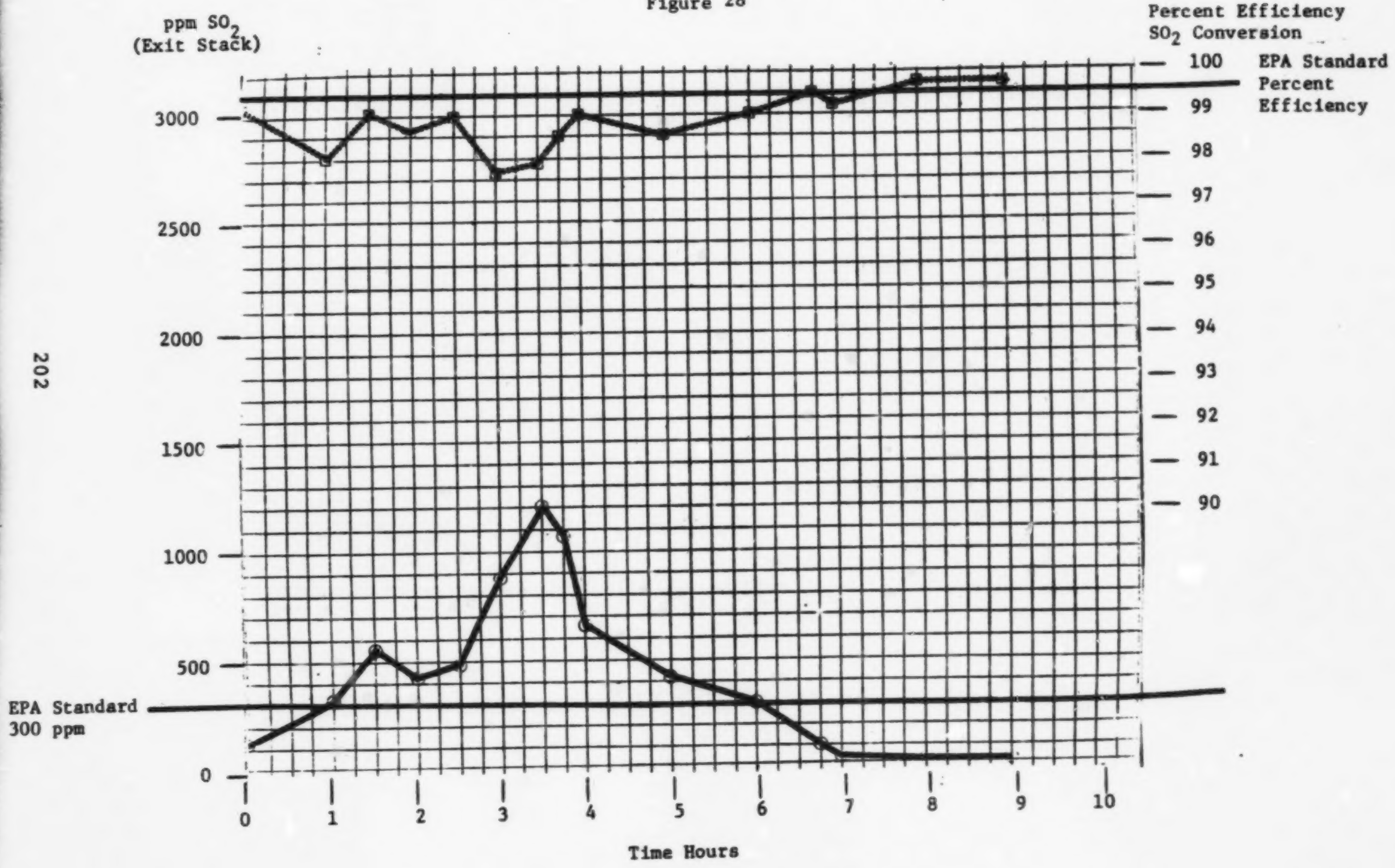
Figure 27



DUAL ABSORPTION PLANT

6 SEPTEMBER 1973
SHUT-DOWN

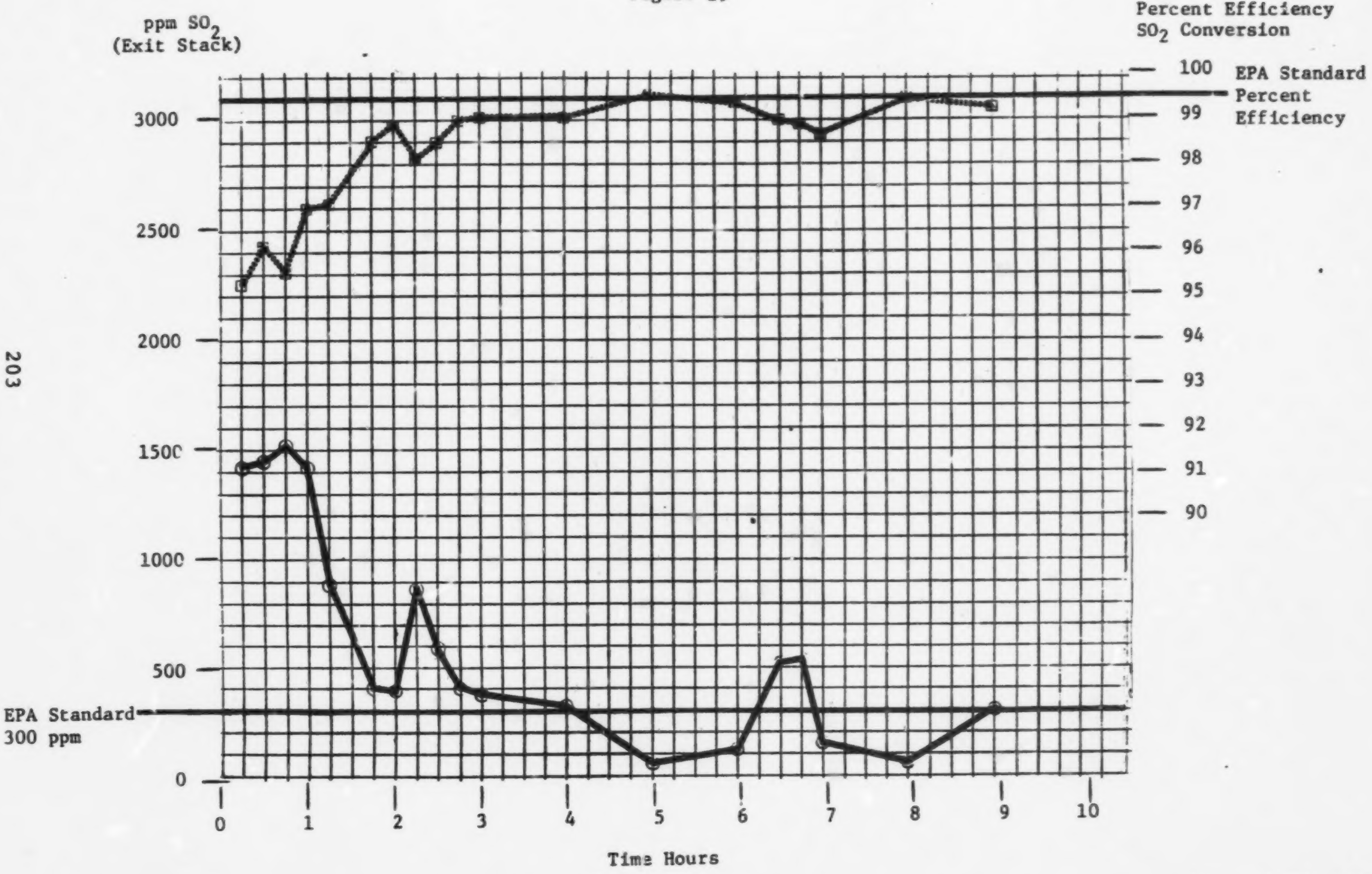
Figure 28



DUAL ABSORPTION PLANT

7 SEPTEMBER 1973

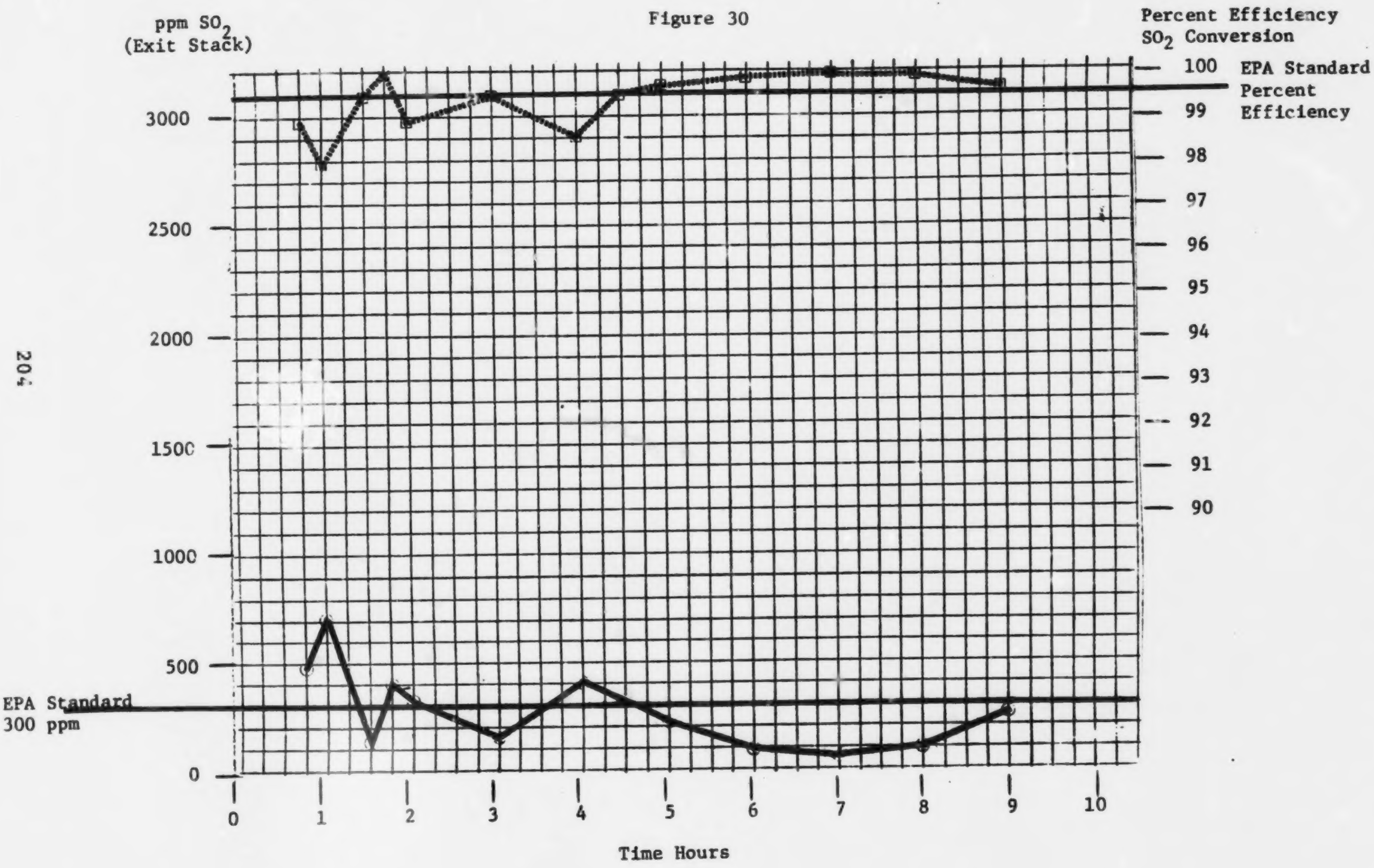
Figure 29



DUAL ABSORPTION PLANT

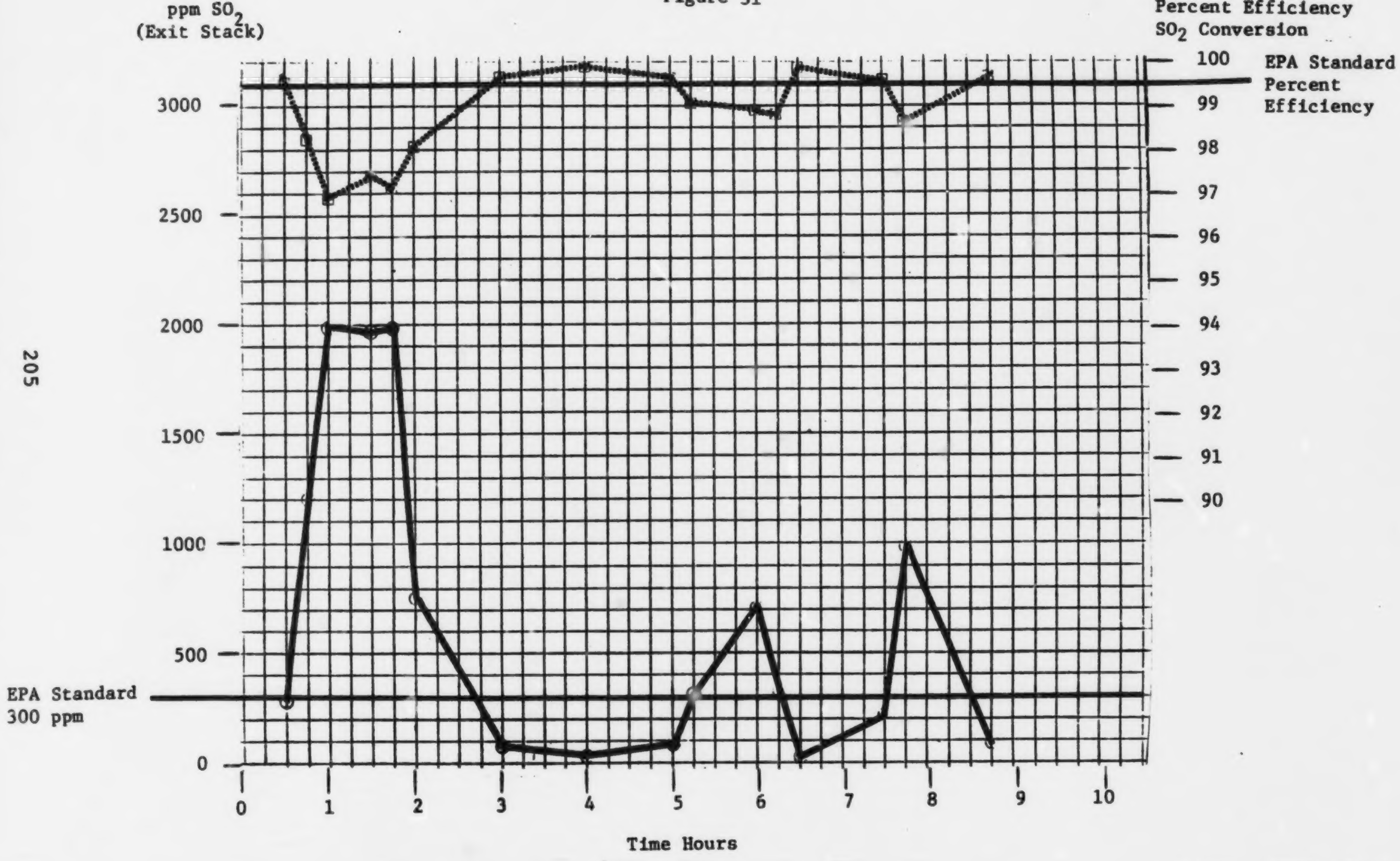
11 SEPTEMBER 1973
START-UP

Figure 30



DUAL ABSORPTION PLANT
16 SEPTEMBER 1973
START-UP

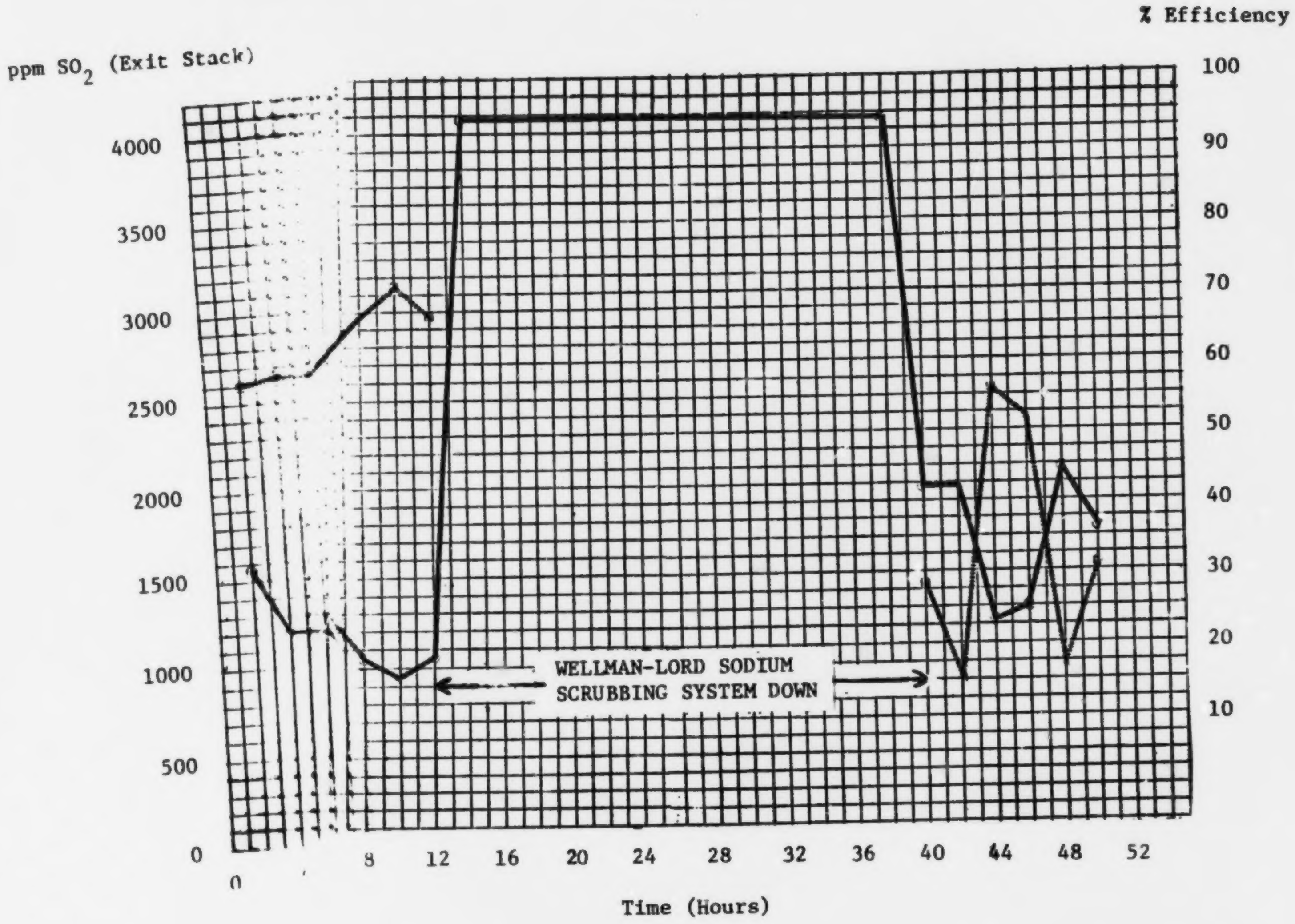
Figure 31



SINGLE ABSORPTION PLANT

START-UP
17 SEPTEMBER 1973

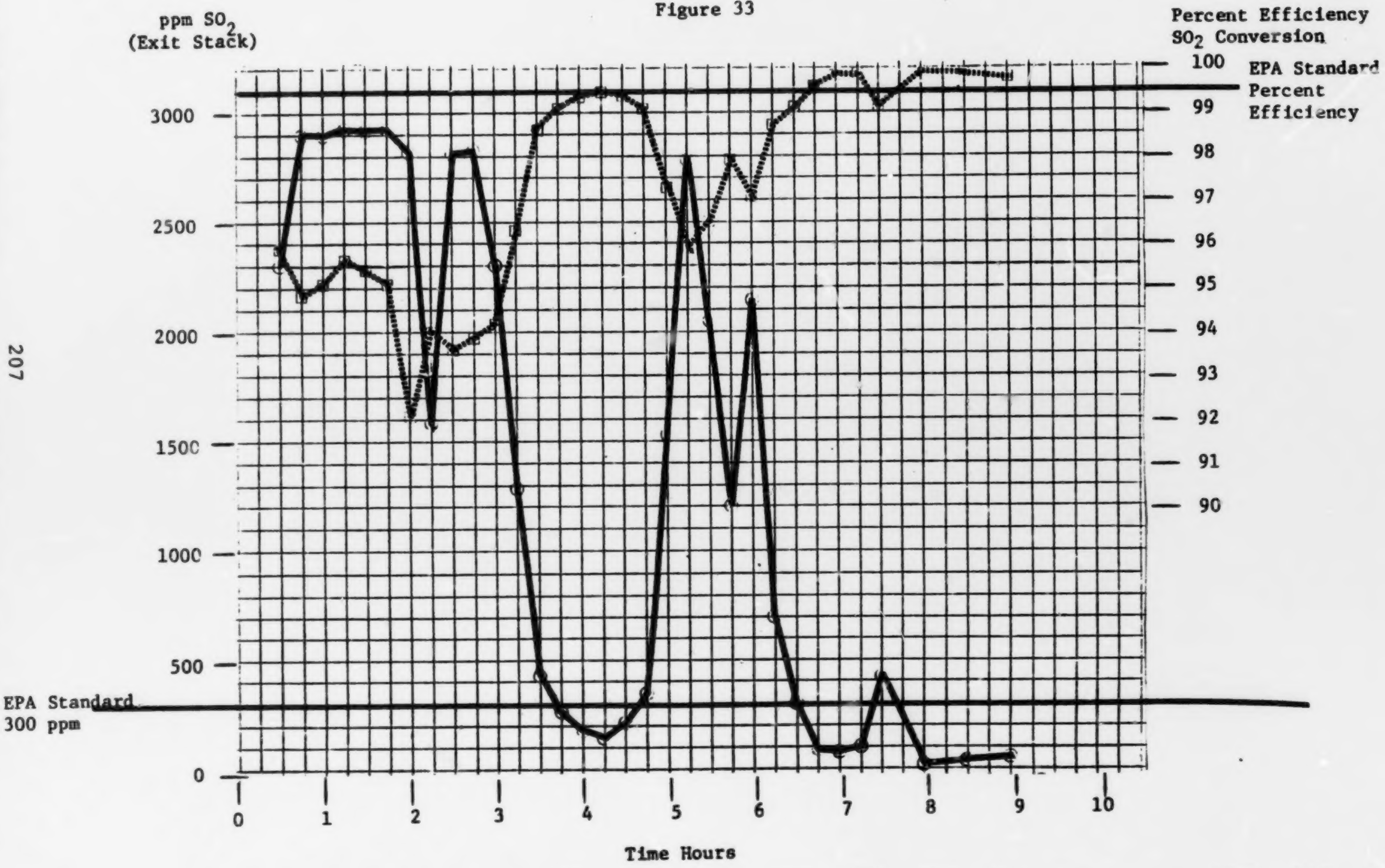
Figure 32



DUAL ABSORPTION PLANT

START-UP
2 OCTOBER 1973

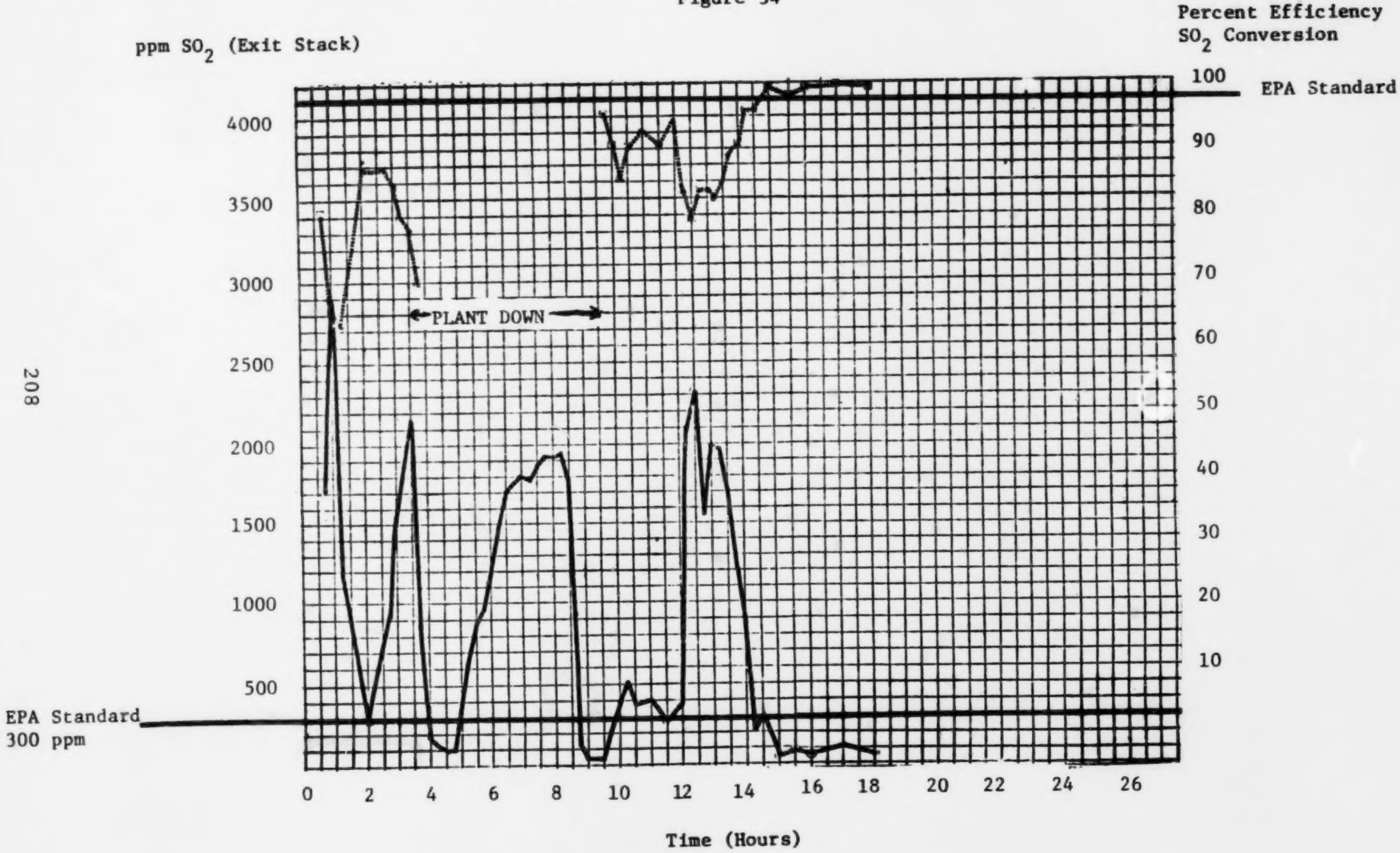
Figure 33



DUAL ABSORPTION PLANT

START-UP
23-24 OCTOBER 1973

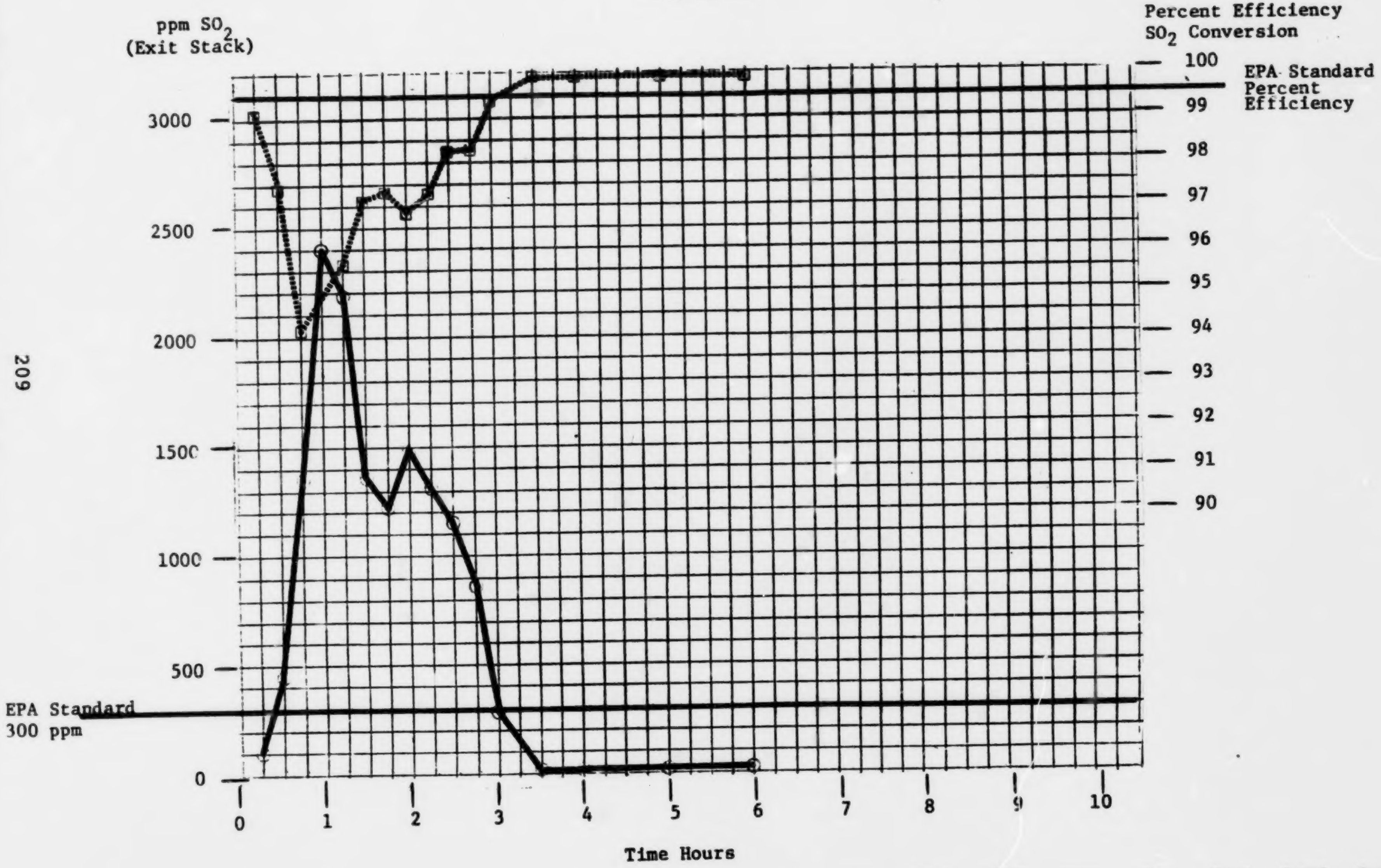
Figure 34



DUAL ABSORPTION PLANT

START-UP
31 OCTOBER 1973

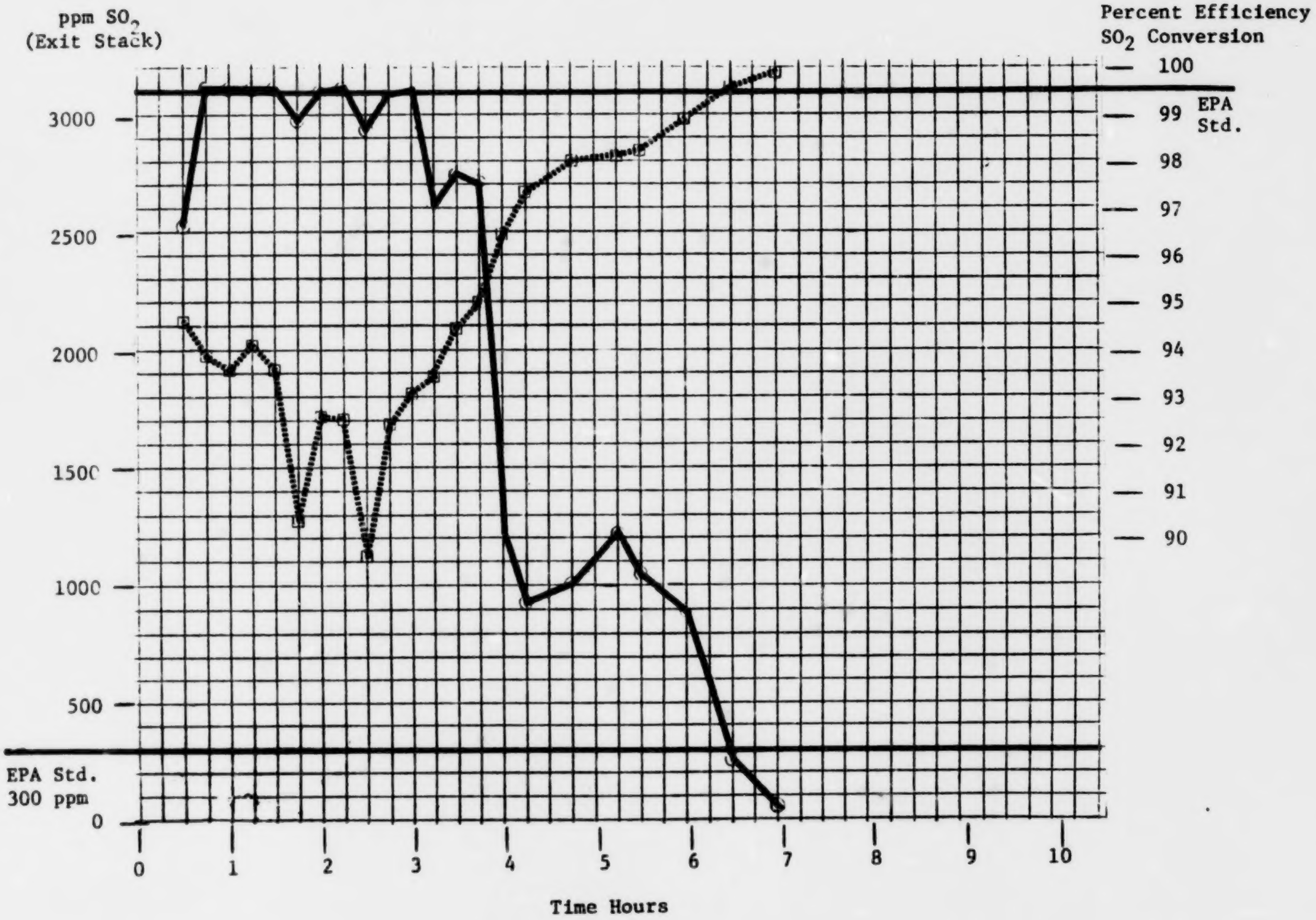
Figure 35



DUAL ABSORPTION PLANT

START-UP
20 NOVEMBER 1973

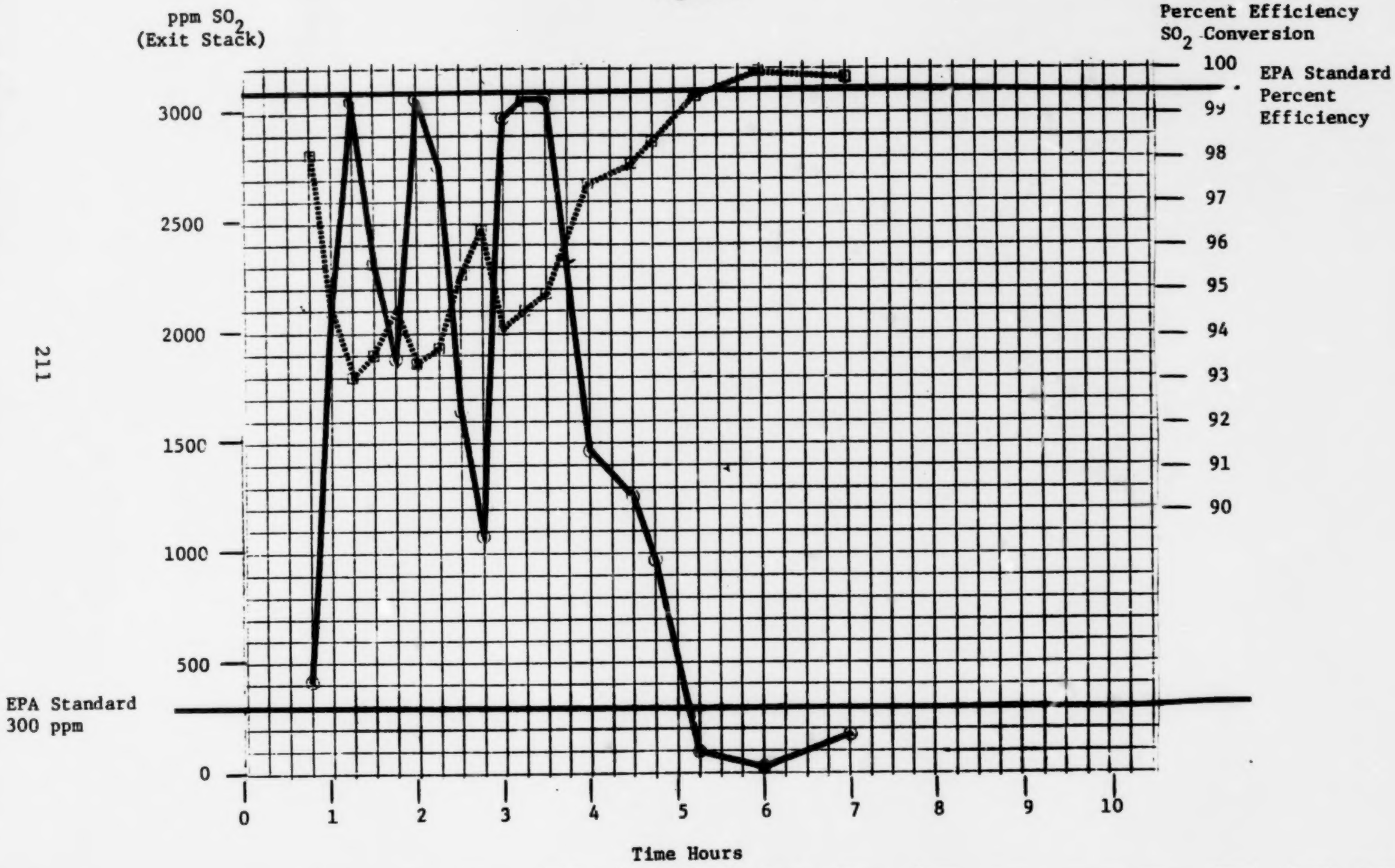
Figure 36



DUAL ABSORPTION PLANT

START-UP
27 NOVEMBER 1973

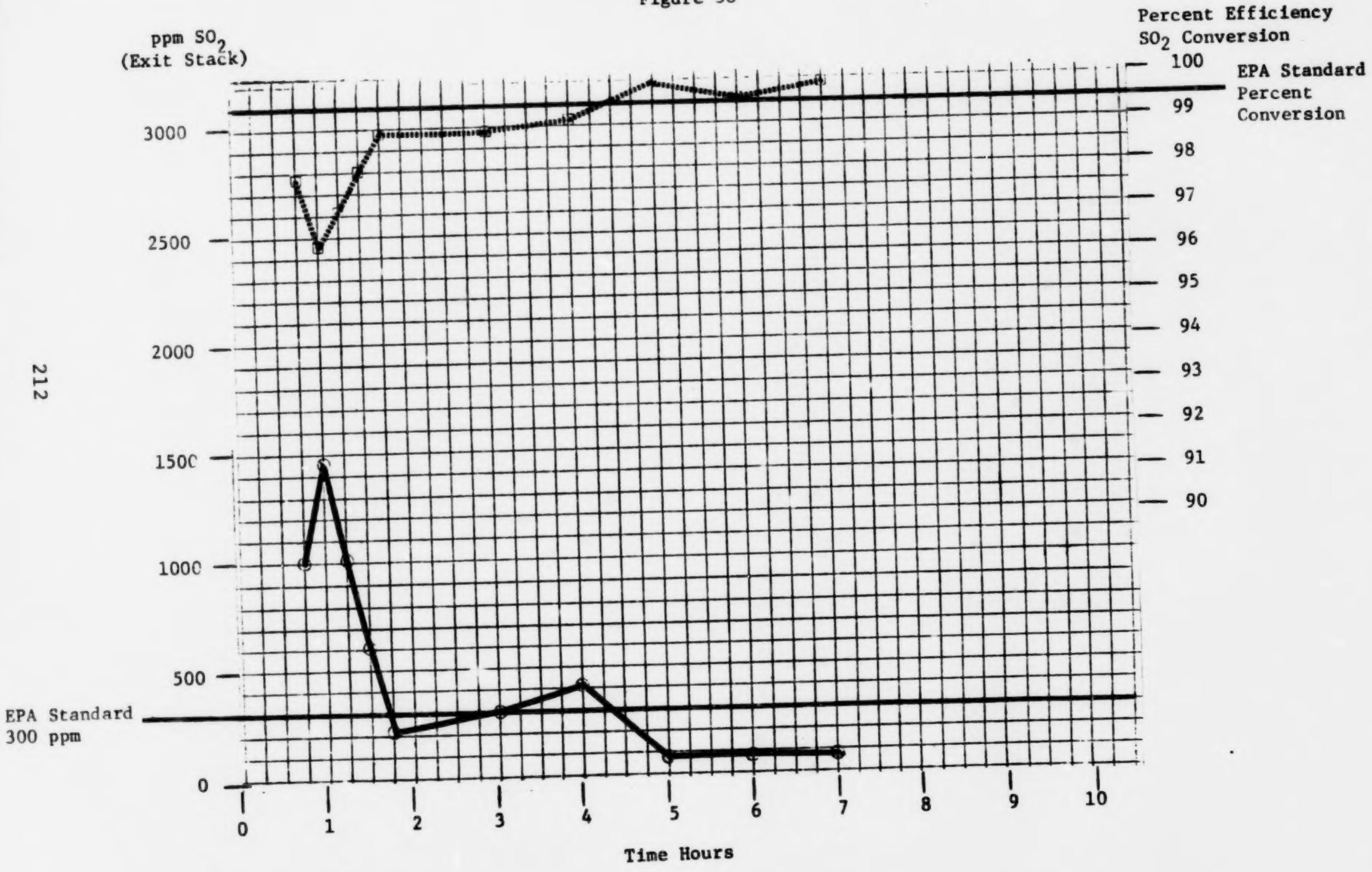
Figure 37



DUAL ABSORPTION PLANT

START-UP
29 NOVEMBER 1973

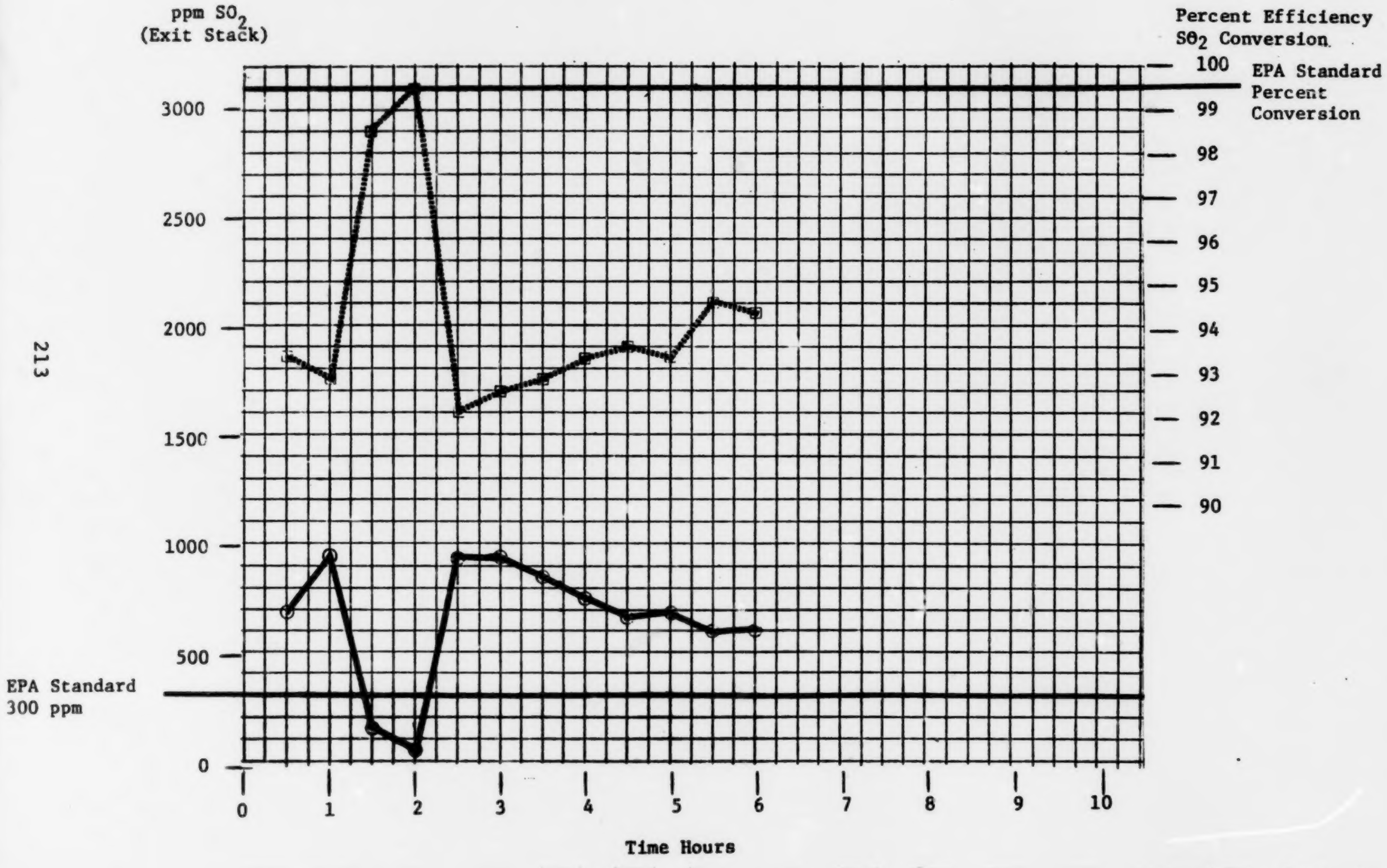
Figure 38



DUAL ABSORPTION PLANT

START-UP
1 DECEMBER 1973

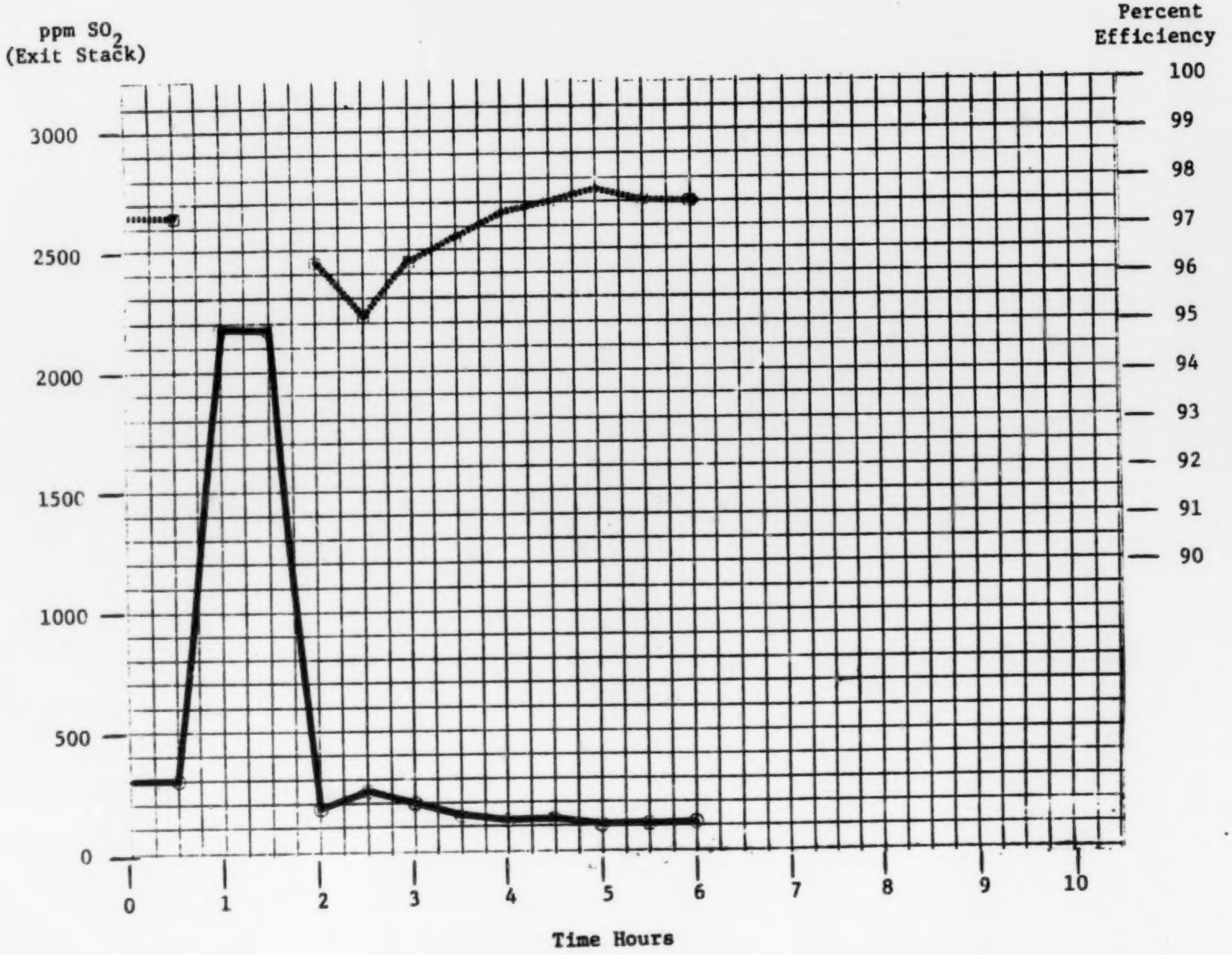
Figure 39



DUAL ABSORPTION PLANT

START-UP OF 30 APRIL AFTER ONE HOUR SHUTDOWN WITH ONE HALF HOUR TO EPA STANDARD

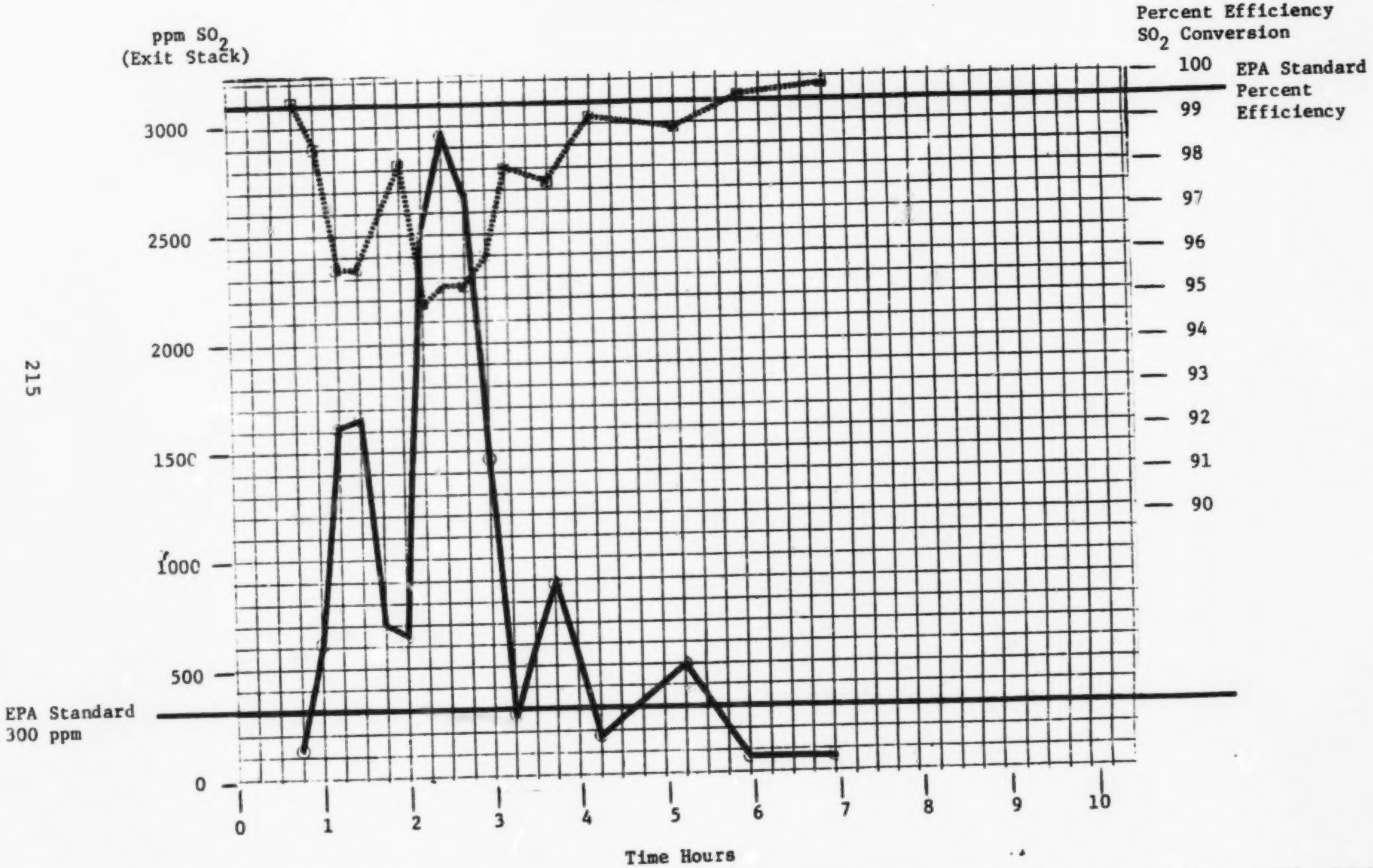
Figure 40



DUAL ABSORPTION PLANT

START-UP
20 OCTOBER 1974

Figure 41



APPENDIX C

STATISTICAL ANALYSIS OF PROCESS PARAMETERS AND EMISSIONS

Table of Contents

Page

Regression Analysis Model of Dual Conversion Acid Plants - Mehta 217

Statistical Analysis of Dual Conversion Acid Plants - Nixon. 296

REGRESSION ANALYSIS MODEL
OF
DUAL CONVERSION ACID PLANTS

Catalytic, Inc.
Project 42466

EPA Contract 68-02-1322

by
Dr. B. M. Mehta

An attempt was made to explain SO_2 emission in terms of process control parameters in H_2SO_4 plant, particularly temperatures of the four catalyst beds in which SO_2 to SO_3 conversion is carried out. Data were collected from two, dual absorption sulfuric acid plants: i) Sulfuric acid plant of ASARCO at ElPaso, Texas, and ii) Texasgulf sulfuric acid plant. Each data point constituted 9 observations. They are: i) parts per million (ppm) of SO_2 - exit stack and ii to ix ($\bar{X}$) Inlet and outlet temperature in ^{o}F of four catalyst beds. For easy interpretation data are divided in two parts. i) start-up and shutdown of plant and ii) normal plant run.

Several models were tried using multiple regression with ppm of SO_2 as the dependent variable and process parameters and their different transforms selected as independent variables. In the following pages each model is described in brief. Complete computer results are attached.

ASARCO Sulfuric Acid Plant

Normal run: Data set (ASAR1) consist of 30 data points selected randomly from normal plant run. Different statistical models were then tried on this set.

Run 1

SO_2 emission as a function of inlet temperature of the four catalyst beds.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x3 + \alpha_3 x5 + \alpha_4 x7$$

The regression was not significant at the 5 per cent level.

Run 2

SO_2 emission as a function of inlet and outlet temperatures of the four catalyst beds.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x2 + \alpha_3 x3 + \alpha_4 x4 + \alpha_5 x5 + \alpha_6 x6 + \alpha_7 x7$$

The regression was not significant at the 5 per cent level.

Run 3

SO_2 emission as a function of inlet temperature of the four beds and temperature rise across each bed.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x3 + \alpha_3 x5 + \alpha_4 x7 + \alpha_5 (x2-x1) + \alpha_6 (x4-x3) + \alpha_7 (x6-x5) + \alpha_8 (x8-x7)$$

The regression was not significant at the 5 percent level.

Run 4

SO_2 emission as a function of temperature increase across the four catalyst beds and temperature drop across inter coolers.

$$Y1 = \alpha_0 + \alpha_1 (x2-x1) + \alpha_2 (x4-x3) + \alpha_3 (x6-x5) + \alpha_4 (x8-x7) + \alpha_5 (x3-x2) + \alpha_6 (x5-x4) + \alpha_7 (x7-x6)$$

The regression was not significant at the 5 per cent level.

Run 5

SO_2 emission as a function of inlet temperature at the four catalyst beds and temperature drop across the three inter coolers.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x3 + \alpha_3 x5 + \alpha_4 x7 + \alpha_5(x3-x2) + \alpha_6(x5-x4) + \alpha_7(x7-x6)$$

The regression was not significant at the 5 per cent level.

Run 6

SO_2 emission as a function of temperature rise across the four catalyst beds and equilibrium constants at the inlet temperature of each bed.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x3 + \alpha_3 x5 + \alpha_4 x7 + \alpha_5(x2-x1) + \alpha_6(x4-x3) + \alpha_7(x6-x5) + \alpha_8(x8-x7)$$

where C = EXP (8929/(460 +x1) - 4.678)

F = EXP (8929/(460 +x3) - 4.678)

I = EXP (8929/(460 +x5) - 4.678)

L = EXP (8929/(460 +x7) - 4.678)

The regression was not significant at the 5 per cent level.

For this data none of the models satisfactorily explain SO_2 emissions in terms of the process parameters, from point of view of 6 significant regressions. Several explanations for lack of fit are: i) variables on the right-hand side are not independent of each other and are highly correlated, ii) there are other process parameters (measured and not measured) which affect the SO_2 emission which were not taken into account; e.g., concentration of H_2SO_4 used in absorption tower, initial concentration of SO_2, furnace temperature and catalyst coins.

It is known that SO_2 to SO_3 conversion is favored by lowering the temperature at which reaction takes place and it is also known that reaction rate is favored by higher reaction temperature. This sets a definite range on the temperature of Catalytic oxidation zones. Thus, to have SO_2 emission below certain set level, the eight temperatures should be controlled within a certain range. To find out this range, 64 data points were randomly selected from the normal plant run (ASAR 3) and standard statistics were calculated. Summary of the calculations is as follows:

Variable	Mean $\bar{X}i$	95% range for xi $\bar{X}i \pm 26$
PPM SO_2 Exist Stack	127	0-307
Temp. (°F) Inlet 1st Converter Bed	824	810-838
Temp. (°F) Outlet 1st Converter Bed	1041	948 - 1133
Temp. (°F) Inlet 2nd Converter Bed	837	819 - 855
Temp. (°F) Outlet 2nd Converter Bed	892	811 - 973
Temp. (°F) Inlet 3rd Converter Bed	786	734 - 838
Temp. (°F) Outlet 3rd Converter Bed	791	737 - 845
Temp. (°F) Inlet 4th Converter Bed	762	704 - 820
Temp. (°F) Outlet 4th Converter Bed	762	702 - 822

It has been found that in this ASARCO plant, SO_2 emission is below EPA limits, if the 8 temperatures stay within above ranges. There are not enough data on the upset condition in order to define the effect of deviation from above temperature range on SO_2 emission from stack.

Start up of ASARCO acid plant: ASARCO plant is not able to control the SO_2 emission during start-up. SO_2 emission appears dependent on length of shutdown time to a certain extent.

It was observed that if shutdown time of the plant is less than two hours, SO_2 emission will not exceed the EPA limit. Above two hours of shutdown time, SO_2 emission is above the EPA limit during start-up. There are 13 data points (STA1) for start-up time and shutdown time. Start-up time is defined as the time in hours which a plant will take to come under the EPA compliance. An attempt was made to find a linear relation between start-up time and shutdown time.

$$\text{Start-up time} = \alpha_0 + \alpha_1 (\text{shutdown time})$$

The regression was not significant at the 5 percent level. Mean and standard deviation were calculated based on this 13 data points. It is calculated that average start-up time is 6.34 hours. For 95 per cent of the time the start-up time should be between 3.14 and 9.54 hours. Not a single data point was more than nine hours. Details of above two runs can be found at the end of this report.

Thirteen data points were selected (ASAR2) having high emission and standard statistics were calculated from these and are compared with one of normal run.

Variable		Mean Normal Run	 Start Up
Y1	(ppm)	127	1678
X1	(^{o}F)	824.0	815.0
X2	(^{o}F)	1040.9	1006.5
X3	(^{o}F)	837.0	811.5
X4	(^{o}F)	892.0	841.0
X5	(^{o}F)	786.0	732.5
X6	(^{o}F)	791.0	729.0
X7	(^{o}F)	762.0	702.0
X8	(^{o}F)	762.0	707.0

Above table clearly shows that four converter beds were not hot enough for proper SO_2 and SO_3 conversion.

TexasGulf Sulfuric Acid Plant

Data set (TGX2) consists of 31 data points selected randomly from large set of normal plant run. Different statistical models were then tried on this set.

Run 1

SO_2 emission as a function of inlet temperature of the four catalyst beds.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x3 + \alpha_3 x5 + \alpha_4 x7$$

The regression was significant at the five per cent level. Hypothesis that α_1 and α_3 are zero cannot be rejected at five per cent level. This reduces the usefulness of the regression model.

Run 2

SO_2 emission as a function of inlet and outlet temperatures of the four catalyst beds.

$$Y1 = \alpha_0 + \alpha_1 x1 + \alpha_2 x2 + \alpha_3 x3 + \alpha_4 x4 + \alpha_5 x5 + \alpha_6 x6 + \alpha_7 x7 + \alpha_8 x8$$

The regression was significant at five percent level. Hypothesis that α_1, α_2, α_3, α_5, α_6 and α_7 are zero, can not be rejected at five percent level. This reduces the usefulness of the regression model.

Run 3

SO_2 emission as a function of log tranform of inlet and outlet temperatures of the four catalyst beds.

$$Y1 = \alpha_0 + \alpha_1 \log x1 + \alpha_2 \log x2 + \alpha_3 \log x3 + \alpha_4 \log x4 + \alpha_5 \log x5 + \alpha_6 \log x6 + \alpha_7 \log x7 + \alpha_8 \log x8$$

The regression is significant at the five percent level. Regression model suffers from same drawbacks as in Run 2.

For this data none of the models satsifactorily explains SO_2 emission in terms of the process parameters, from point of view of three significant regression. Same reasons can be sited here as before (for ASARCO Data) for not getting a useful model from a predictive stand point of view.

Due to lack of model, an attempt was made to define a temperature range for each of the eight temperatures such that SO_2 emission will be below the EPA limits. Thirty data points were selected randomly (Tαx4) from normal plant run and standard statistics were calculated. Summary of results is as follows.

Variable	$\bar{x}$ Mean	95% Range for xi Mean ± 26
PPM SO_2 Exit Stack	128	56 - 200
Temp. (°F) Inlet 1st Converter Bed	802	702 - 814
Temp. (°F) Outlet 1st Converter Bed	1117	1095 - 1139
Temp. (°F) Inlet 2nd Converter Bed	841	817 - 865
Temp. (°F) Outlet 2nd Converter Bed	977	903 - 1051
Temp. (°F) Inlet 3rd Converter Bed	812	784 - 840
Temp. (°F) Outlet 3rd Converter Bed	848	797 - 899
Temp. (°F) Inlet 4th Converter Bed	816	788 - 844
Temp. (°F) Outlet 4th Converter Bed	841	809 - 873

It has been found that SO_2 emission will be below the EPA limitations if the eight process temperatures remain within the respective ranges.

The plant has a capability of heating the catalyst beds to a proper temperature before passing SO_2 through catalyst; because of this they are able to control the emission during start up.

RECOMMENDATION FOR FUTURE DATA COLLECTION AND ANALYSIS:

At every point of analysis it was felt that there is a lack of total number of complete data points. Large number of data points were incomplete, meaning one or more process variables were not recorded. There were no data to compare the two plants of the same design. To make any conclusive statements data should be collected from at least three plants of same design. Record of each higher SO_2 emission should be kept. This record of upset conditions will help us narrow the temperature range for eight variables (X1, X2-X8) and define the exact variable with its magnitude which caused the higher emission. It will be easier for the regulatory agency to pinpoint whether a particular upset condition was legitimate or not. Reliability of SO_2 analyzer should be checked very often to ensure us of correct data.

Nomenclature Used in Regression Analysis

Y1 = PPM SO_2 Exit Stack

X1 = Temp (^{o}F) Inlet 1st Converter Bed

X2 = Temp (^{o}F) Outlet 1st Converter Bed

X3 = Temp (^{o}F) Inlet 2nd Converter Bed

X4 = Temp (^{o}F) Outlet 2nd Converter Bed

X5 = Temp (^{o}F) Inlet 3rd Converter Bed

X6 = Temp (^{o}F) Outlet 3rd Converter Bed

X7 = Temp (^{o}F) Inlet 4th Converter Bed

X8 = Temp (^{o}F) Outlet 4th Converter Bed

MULTIPLE REGRESSION ANALYSIS
ASARCO PLANT NORMAL OPERATION

ASARCO

Data Set 1

ASAR1

```
READY
LIST ASAR1

ASAR1           11:07EST      11/25/74
     Y1  x1   x2   x3   x4   x5   x6   x7   x8
100 191,825,1100,850,975,835,860,825,795
101 145,810,1030,830,890,785,800,765,760
102 274,815,1100,840,945,820,850,825,820
103 228,818,1058,842,934,826,810,798,782
104 156,830,1100,830,900,760,780,755,780
105 701,825,955,820,845,730,725,705,710
106 95,830,1000,830,860,795,780,740,730
108 138,830,1070,845,930,805,840,785,775
109 239,825,1120,840,940,800,835,795,810
110 145,820,1075,845,945,835,840,825,815
111 112,815,1100,850,955,820,850,825,820
112 129,830,1000,850,900,790,790,745,750
113 149,825,1080,845,950,835,840,820,825
114 222,825,1070,830,955,825,790,770,755
115 259,820,1055,835,915,780,780,760,755
116 173,815,1075,835,895,775,800,765,770
117 331,830,1060,830,910,770,790,770,780
118 327,830,1010,835,870,765,785,750,765
119 388,830,1110,850,930,800,815,765,770
120 229,810,1000,840,890,825,840,815,800
121 255,825,1080,820,885,720,690,675,685
122 257,835,1035,840,865,780,790,770,760
123 223,825,1090,840,895,785,805,770,780
124 297,820,1010,835,940,770,780,765,750
125 374,815,1065,835,910,780,790,760,770
126 353,814,960,834,883,796,804,788,770
127 181,812,1118,834,936,780,800,752,754
128 182,824,1114,834,922,768,775,758,764
129 102,824,1136,840,962,800,830,782,782
```

RUN 1

```
MULTIPLE REGRESSION PROGRAM

   XMEAN            YMEAN
                 2.363793E+02
 8.224828E+02
 1.061241E+03
 8.373793E+02
 9.148966E+02
 7.915517E+02
 8.022069E+02
 7.732069E+02
 7.717931E+02



  OBSERVED          CALCULATED        EST VAR
1.9100000E+02     1.4841158E+02     1.9074241E+03
1.4500000E+02     2.6274889E+02     2.3663184E+03
2.7400000E+02     2.1089986E+02     2.1450056E+03
2.2800000E+02     1.6604196E+02     1.5383148E+03
1.5600000E+02     3.1621091E+02     2.4381770E+03
7.0100000E+02     3.6632825E+02     2.9301543E+03
9.5000000E+01     2.2258276E+02     4.0136465E+03
1.3800000E+02     1.9546666E+02     1.3826847E+03
2.3900000E+02     2.3063944E+02     1.0300517E+03
1.4500000E+02     1.6267472E+02     1.5902827E+03
1.1200000E+02     1.7914977E+02     2.7250538E+03
1.2900000E+02     1.7519773E+02     5.5225457E+03
1.4900000E+02     1.5949214E+02     1.8744414E+03
2.2200000E+02     1.8181375E+02     6.4185410E+03
2.5900000E+02     2.5662385E+02     6.5617222E+02
1.7300000E+02     2.7112709E+02     1.4858165E+03
3.3100000E+02     3.0795304E+02     3.1945885E+03
3.2700000E+02     2.8422071E+02     1.3731419E+03
3.8800000E+02     1.7173433E+02     1.5124348E+03
2.2900000E+02     1.8837831E+02     2.2762290E+03
2.5500000E+02     3.6020267E+02     4.2575563E+03
2.5700000E+02     2.5517351E+02     2.4709890E+03
2.2300000E+02     2.4062902E+02     7.3542339E+02
2.9700000E+02     2.8405968E+02     1.2105110E+03
3.7400000E+02     2.5501194E+02     1.3776373E+03
3.5300000E+02     2.4848755E+02     1.3649071E+03
1.8100000E+02     2.4954862E+02     2.4464908E+03
1.8200000E+02     2.8634020E+02     9.6137556E+02
1.0200000E+02     2.1785139E+02     5.3500893E+02
```

RUN 1 (Continued)

```
   ...............................................................
   .             .DEGREE ØF FREE.  SUM ØF SQUARES. VARIANCE ESTIMATE .
   . REGRESSIØN.        4       .  9.752241E+04  .  2.438060E+04     .
   . REMAINDER .       24       .  3.155564E+05  .  1.314818E+04     .
   . TØTAL     .       28       .  4.130788E+05  .                   .
   ...............................................................

MULTIPLE CØRRELATIØN CØEFFICIENT =  4.858875E-01

CØNSTANT TERM(INTERCEPT) =  3.680666E+03


    CØEFFICIENTS      EST ØF SD
   3.2238233E-01    3.5627722E+00
  -3.1750097E+00    4.4162024E+00
  -2.2641340E+00    1.7134936E+00
   9.5889744E-01    1.4836531E+00


 F RATIØ(  4, 24  DEGREES ØF FREEDØM)=  1.854294E+00

UPPER RT HAND PØRTIØN ØF MATRICES ØNLY

INVERSE ADJ DATA MØMENT MATRIX
RØW(  1)  9.6541E-04 -4.6081E-04  9.7809E-07  1.3341E-04
RØW(  2)  1.4833E-03 -1.5673E-04 -1.5615E-04
RØW(  3)  2.2331E-04 -1.4045E-04
RØW(  4)  1.6742E-04

EST CØEFFICIENT VAR-CØVAR MATRIX
RØW(  1)  1.2693E+01 -6.0588E+00  1.2860E-02  1.7541E+00
RØW(  2)  1.9503E+01 -2.0608E+00 -2.0530E+00
RØW(  3)  2.9361E+00 -1.8467E+00
RØW(  4)  2.2012E+00

ADJ DATA CØRRELATIØN MATRIX
RØW(  1)  1.0000E+00 -3.8508E-01  2.1066E-03  3.3184E-01
RØW(  2)  1.0000E+00 -2.7233E-01 -3.1334E-01
RØW(  3)  1.0000E+00 -7.2642E-01
RØW(  4)  1.0000E+00
```

RUN 2

```
 MULTIPLE REGRESSION PROGRAM

     XMEAN          YMEAN
                  2.363793E+02
  8.224828E+02
  1.061241E+03
  8.373793E+02
  9.148966E+02
  7.915517E+02
  8.022069E+02
  7.732069E+02
  7.717931E+02


NUMBER, INDICES OF VARIATES DESIRED?8,1,2,3,4,5,6,7,8


WANT TO SEE PREDICTED VALUES, YES OR NO?YES


    OBSERVED          CALCULATED        EST VAR
  1.9100000E+02    1.3405888E+02    5.1931016E+03
  1.4500000E+02    2.5402067E+02    3.1793207E+03
  2.7400000E+02    1.8126159E+02    2.2841035E+03
  2.2800000E+02    1.8290439E+02    3.2397968E+03
  1.5600000E+02    2.7816802E+02    3.6382258E+03
  7.0100000E+02    4.4280215E+02    4.2805878E+03
  9.5000000E+01    2.1989134E+02    5.9655442E+03
  1.3800000E+02    1.8402139E+02    4.1270549E+03
  2.3900000E+02    1.8837903E+02    2.7757467E+03
  1.4500000E+02    1.7634925E+02    2.3800124E+03
  1.1200000E+02    1.7855814E+02    2.9965314E+03
  1.2900000E+02    2.6600659E+02    7.8335695E+03
  1.4900000E+02    1.3582841E+02    4.2692028E+03
  2.2200000E+02    1.7884315E+02    7.3538857E+03
  2.5900000E+02    2.6621957E+02    1.1255771E+03
  1.7300000E+02    2.3084653E+02    2.1972758E+03
  3.3100000E+02    3.2133859E+02    3.4886685E+03
  3.2700000E+02    3.2950727E+02    2.9602452E+03
  3.8800000E+02    1.3395846E+02    3.7527185E+03
  2.2900000E+02    2.2523835E+02    4.0416290E+03
  2.5500000E+02    3.1475504E+02    6.6574217E+03
  2.5700000E+02    2.5227908E+02    6.9751483E+03
  2.2300000E+02    1.9552913E+02    2.0111006E+03
  2.9700000E+02    3.7997648E+02    6.6555059E+03
  3.7400000E+02    2.5136933E+02    2.0302288E+03
  3.5300000E+02    3.3747058E+02    3.5187125E+03
  1.8100000E+02    1.7319633E+02    4.3945007E+03
  1.8200000E+02    2.3921095E+02    2.5866204E+03
  1.0200000E+02    1.5301146E+02    3.0770284E+03
```

RUN 2 (Continued)

```
...............................................................
.              .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
. REGRESSION.        8       .  1.575476E+05  .  1.969345E+04     .
. REMAINDER .       20       .  2.555312E+05  .  1.277656E+04     .
. TOTAL     .       28       .  4.130788E+05  .                   .
...............................................................

MULTIPLE CORRELATION COEFFICIENT =  6.175746E-01

CONSTANT TERM(INTERCEPT) =  2.512162E+03


    COEFFICIENTS      EST OF SD
  8.1945439E-01    3.6111681E+00
 -1.3987151E+00    8.3710714E-01
 -1.3202066E+00    5.0597878E+00
  1.0498617E+00    1.3460586E+00
 -2.6366182E+00    2.0017645E+00
 -7.5009784E-01    2.2222179E+00
  7.0603361E-01    3.4613877E+00
  1.0656316E+00    2.6875709E+00


  F RATIO(  8, 20  DEGREES OF FREEDOM)=  1.541373E+00

 UPPER RT HAND PORTION OF MATRICES ONLY

 INVERSE ADJ DATA MOMENT MATRIX
 ROW(   1)  1.0207E-03 -1.8554E-05 -5.2963E-04  4.0818E-05 -6.8396E-05
  7.7021E-05  1.9408E-04 -1.0449E-04
 ROW(   2)  5.4846E-05  3.6579E-05 -6.7828E-05  1.1669E-05 -3.5251E-05
  1.1361E-04 -8.8688E-05
 ROW(   3)  2.0038E-03 -8.7455E-05 -8.4696E-05 -4.2333E-04  1.8356E-04
 -3.1409E-05
 ROW(   4)  1.4181E-04 -4.0494E-05  4.3142E-05 -1.3490E-04  9.4492E-05
 ROW(   5)  3.1363E-04 -8.3843E-05 -2.5782E-04  1.6258E-04
 ROW(   6)  3.8651E-04 -2.1693E-04 -4.7980E-05
 ROW(   7)  9.3775E-04 -5.7385E-04
 ROW(   8)  5.6533E-04

 EST COEFFICIENT VAR-COVAR MATRIX
 ROW(   1)  1.3041E+01 -2.3706E-01 -6.7669E+00  5.2152E-01 -8.7386E-01
  9.8406E-01  2.4797E+00 -1.3350E+00
 ROW(   2)  7.0075E-01  4.6735E-01 -8.6661E-01  1.4910E-01 -4.5038E-01
  1.4515E+00 -1.1331E+00
 ROW(   3)  2.5601E+01 -1.1174E+00 -1.0821E+00 -5.4087E+00  2.3453E+00
 -4.0130E-01
 ROW(   4)  1.8119E+00 -5.1738E-01  5.5121E-01 -1.7235E+00  1.2073E+00
 ROW(   5)  4.0071E+00 -1.0712E+00 -3.2941E+00  2.0772E+00
 ROW(   6)  4.9383E+00 -2.7716E+00 -6.1302E-01
 ROW(   7)  1.1981E+01 -7.3319E+00
 ROW(   8)  7.2230E+00
```

RUN 2 (Continued)

```
ADJ DATA CORRELATION MATRIX
ROW(  1)  1.0000E+00 -7.8420E-02 -3.7035E-01  1.0729E-01 -1.2089E-01
 1.2263E-01  1.9838E-01 -1.3755E-01
ROW(  2)  1.0000E+00  1.1034E-01 -7.6909E-01  8.8976E-02 -2.4211E-01
 5.0096E-01 -5.0366E-01
ROW(  3)  1.0000E+00 -1.6406E-01 -1.0684E-01 -4.8103E-01  1.3391E-01
-2.9511E-02
ROW(  4)  1.0000E+00 -1.9201E-01  1.8427E-01 -3.6992E-01  3.3372E-01
ROW(  5)  1.0000E+00 -2.4081E-01 -4.7541E-01  3.8611E-01
ROW(  6)  1.0000E+00 -3.6033E-01 -1.0264E-01
ROW(  7)  1.0000E+00 -7.8814E-01
ROW(  8)  1.0000E+00
```

RUN 3

```
MULTIPLE REGRESSION PROGRAM

   XMEAN           YMEAN
                 2.363793E+02
 6.224328E+02
 8.373793E+02
 7.915517E+02
 7.732069E+02
 2.387586E+02
 7.751724E+01


  OBSERVED          CALCULATED        EST VAR
 1.9100000E+02     1.3405887E+02     5.1930969E+03
 1.4500000E+02     2.5402068E+02     3.1793200E+03
 2.7400000E+02     1.8126160E+02     2.2841037E+03
 2.2800000E+02     1.6290439E+02     3.2397977E+03
 1.5600000E+02     2.7816805E+02     3.6382273E+03
 7.0100000E+02     4.4280216E+02     4.2805889E+03
 9.5000000E+01     2.1989136E+02     5.9655428E+03
 1.3800000E+02     1.8402140E+02     4.1270532E+03
 2.3900000E+02     1.8837906E+02     2.7757466E+03
 1.4500000E+02     1.7634926E+02     2.3800136E+03
 1.1200000E+02     1.7855814E+02     2.9965323E+03
 1.2900000E+02     2.6600661E+02     7.8335696E+03
 1.4900000E+02     1.8582843E+02     4.2692042E+03
 2.2200000E+02     1.7884317E+02     7.3538864E+03
 2.5900000E+02     2.6621957E+02     1.1255772E+03
 1.7300000E+02     2.3084654E+02     2.1972754E+03
 3.3100000E+02     3.2133860E+02     3.4886690E+03
 3.2700000E+02     3.2950730E+02     2.9602454E+03
 3.8800000E+02     1.3395848E+02     3.7527186E+03
 2.2900000E+02     2.2523836E+02     4.0416292E+03
 2.5500000E+02     3.1475504E+02     6.6574232E+03
 2.5700000E+02     2.5227906E+02     6.9751463E+03
 2.2300000E+02     1.9552914E+02     2.0111008E+03
 2.9700000E+02     3.7997647E+02     6.6555047E+03
 3.7400000E+02     2.5136935E+02     2.0302290E+03
 3.5300000E+02     3.3747058E+02     3.5187122E+03
 1.8100000E+02     1.7319634E+02     4.3944999E+03
 1.8200000E+02     2.3921095E+02     2.5866209E+03
 1.0200000E+02     1.5301148E+02     3.0770275E+03
```

RUN 3 (Continued)

```
 ..............................................................................
 .               .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
 . REGRESSION.          8       .  1.575476E+05  .  1.969345E+04      .
 . REMAINDER .         20       .  2.555312E+05  .  1.277656E+04      .
 . TOTAL     .         28       .  4.130788E+05  .                    .
 ..............................................................................

MULTIPLE CORRELATION COEFFICIENT =  6.175746E-01

CONSTANT TERM(INTERCEPT) =  2.512162E+03


   COEFFICIENTS     EST OF SD
 -5.7926065E-01   3.6424122E+00
 -2.7034557E-01   5.0178258E+00
 -3.3867151E+00   2.6082259E+00
  1.7716646E+00   2.1308535E+00
 -1.3987152E+00   8.3710711E-01
  1.0498619E+00   1.3460587E+00
 -7.5009738E-01   2.2222179E+00
  1.0656326E+00   2.6875702E+00


  F RATIO( 8, 20  DEGREES OF FREEDOM)=  1.541373E+00

 UPPER RT HAND PORTION OF MATRICES ONLY

 INVERSE ADJ DATA MOMENT MATRIX
 ROW(  1)  1.0384E-03 -5.2006E-04 -1.4956E-05  1.1451E-04  3.6292E-05
 -2.7010E-05  4.1770E-05 -1.9318E-04
 ROW(  2)  1.9707E-03 -5.0537E-04  1.1174E-04 -3.1249E-05  5.4357E-05
 -3.8018E-04  6.3082E-05
 ROW(  3)  5.3245E-04 -3.6015E-04 -2.3581E-05  2.6477E-06  3.0267E-04
  1.1460E-04
 ROW(  4)  3.5538E-04  2.4922E-05 -4.0406E-05 -2.6491E-04 -8.5167E-06
 ROW(  5)  5.4846E-05 -6.7828E-05 -3.5251E-05 -8.8688E-05
 ROW(  6)  1.4181E-04  4.3142E-05  9.4491E-05
 ROW(  7)  3.8651E-04 -4.7980E-05
 ROW(  8)  5.6533E-04

 EST COEFFICIENT VAR-COVAR MATRIX
 ROW(  1)  1.3267E+01 -6.6446E+00 -1.9109E-01  1.4631E+00  4.6369E-01
 -3.4510E-01  5.3368E-01 -2.4681E+00
 ROW(  2)  2.5179E+01 -6.4569E+00  1.4277E+00 -3.9926E-01  6.9450E-01
 -4.8574E+00  8.0597E-01
 ROW(  3)  6.8029E+00 -4.6015E+00 -3.0129E-01  3.3829E-02  3.8670E+00
  1.4642E+00
 ROW(  4)  4.5405E+00  3.1842E-01 -5.1625E-01 -3.3847E+00 -1.0881E-01
 ROW(  5)  7.0075E-01 -8.6661E-01 -4.5038E-01 -1.1331E+00
 ROW(  6)  1.8119E+00  5.5121E-01  1.2073E+00
 ROW(  7)  4.9383E+00 -6.1302E-01
 ROW(  8)  7.2230E+00
```

RUN 3 (Continued)

```
ADJ DATA CORRELATION MATRIX
ROW(  1)  1.0000E+00 -3.6355E-01 -2.0114F-02  1.3851E-01  1.5208F-01
-7.0386E-02  6.5933F-02 -2.5213E-01
ROW(  2)  1.0000E+00 -4.9336F-01  1.3353F-01 -9.5052F-02  1.0282F-01
-4.3562E-01  5.9765E-02
ROW(  3)  1.0000F+00 -8.2795F-01 -1.3799F-01  9.6356E-03  6.6718F-01
 2.0888E-01
ROW(  4)  1.0000E+00  1.7851F-01 -1.7999F-01 -7.1473F-01 -1.9001F-02
ROW(  5)  1.0000E+00 -7.6909F-01 -2.4211F-01 -5.0366F-01
ROW(  6)  1.0000F+00  1.8427F-01  3.3372F-01
ROW(  7)  1.0000E+00 -1.0264E-01
ROW(  8)  1.0000F+00
```

RUN 4

```
MULTIPLE REGRESSION PROGRAM

      XMEAN          YMEAN
                   2.363793E+02
    2.387586E+02
    7.751724E+01
    1.065517E+01
   -1.413793E+00
   -2.238621E+02
   -1.233448E+02
   -2.900000E+01



NUMBER, INDICES OF VARIATES DESIRED?7,1,2,3,4,5,6,7


WANT TO SEE PREDICTED VALUES, YES OR NO?YES


     OBSERVED          CALCULATED        EST VAR
   1.9100000E+02     1.4576747E+02     4.5900233E+03
   1.4500000E+02     2.2822065E+02     9.7821996E+02
   2.7400000E+02     1.7170387E+02     1.9210613E+03
   2.2800000E+02     1.8901328E+02     3.0153719E+03
   1.5600000E+02     2.7916687E+02     3.5150346E+03
   7.0100000E+02     4.3310248E+02     3.8430605E+03
   9.5000000E+01     2.1394675E+02     5.6574145E+03
   1.3800000E+02     1.8950993E+02     3.8960092E+03
   2.3900000E+02     1.8618751E+02     2.6690311E+03
   1.4500000E+02     1.8374593E+02     2.1291872E+03
   1.1200000E+02     1.8582575E+02     2.7313220E+03
   1.2900000E+02     2.9016183E+02     5.7376433E+03
   1.4900000E+02     1.9572399E+02     3.8199624E+03
   2.2200000E+02     1.7088799E+02     6.9119391E+03
   2.5900000E+02     2.6667511E+02     1.0877826E+03
   1.7300000E+02     2.1915545E+02     1.6943443E+03
   3.3100000E+02     3.2208684E+02     3.3717892E+03
   3.2700000E+02     3.3443362E+02     2.7861410E+03
   3.8800000E+02     1.5306648E+02     2.4790886E+03
   2.2900000E+02     2.1197438E+02     3.3542331E+03
   2.5500000E+02     3.1239980E+02     6.4202791E+03
   2.5700000E+02     2.7538743E+02     5.0633582E+03
   2.2300000E+02     2.0064470E+02     1.8623307E+03
   2.9700000E+02     3.8245955E+02     6.4164783E+03
   3.7400000E+02     2.4178304E+02     1.6738419E+03
   3.5300000E+02     3.2762712E+02     3.0974757E+03
   1.8100000E+02     1.5179771E+02     2.8075017E+03
   1.8200000E+02     2.4451697E+02     2.4126092E+03
   1.0200000E+02     1.4802752E+02     2.8972714E+03
```

RUN 4 (Continued)

```
.....................................................................
.             .DEGREE ØF FREE.  SUM ØF SQUARES. VARIANCE ESTIMATE .
. REGRESSIØN.        7       .  1.536243E+05  .  2.194633E+04     .
. REMAINDER .       21       .  2.594545E+05  .  1.235498E+04     .
. TØTAL     .       28       .  4.130788E+05  .                   .
.....................................................................

MULTIPLE CØRRELATIØN CØEFFICIENT =  6.098366E-01

CØNSTANT TERM(INTERCEPT) =  4.641007E+02

   CØEFFICIENTS      EST ØF SD
 -1.7928644E+00   3.1026344E+00
 -7.8321091E-01   1.6550263E+00
  8.9553101E-01   1.6031329E+00
  1.0274120E+00   2.6419875E+00
 -4.0431112E-01   3.1277579E+00
 -1.8165000E+00   1.3935297E+00
  2.1242252E+00   1.9998195E+00
```

```
F RATIØ(  7, 21  DEGREES ØF FREEDØM)=  1.776315E+00

UPPER RT HAND PØRTIØN ØF MATRICES ØNLY

INVERSE ADJ DATA MOMENT MATRIX
RØW(  1)  7.7915E-04 -1.9313E-04 -1.9788E-04  9.5005E-05  7.5807E-04
-1.4820E-04 -2.1168E-06
RØW(  2)  2.2170E-04  2.8712E-05  1.9845E-04 -1.2721E-04  1.1857E-0
-2.5587E-05
RØW(  3)  2.0802E-04 -5.7725E-05 -1.8788E-04  2.6509E-05  1.0179E-04
RØW(  4)  5.6496E-04  1.8359E-04  1.0412E-04 -5.0821E-06
RØW(  5)  7.9182E-04 -1.5006E-04 -2.6126E-05
RØW(  6)  1.5718E-04  1.3330E-05
RØW(  7)  3.2370E-04

EST CØEFFICIENT VAR-CØVAR MATRIX
RØW(  1)  9.6263E+00 -2.3861E+00 -2.4448E+00  1.1738E+00  9.3660E+00
-1.8310E+00 -2.6153E-02
RØW(  2)  2.7391E+00  3.5474E-01  2.4519E+00 -1.5716E+00  1.4649E+0
-3.1613E-01
RØW(  3)  2.5700E+00 -7.1319E-01 -2.3213E+00  3.2751E-01  1.2577E+0
RØW(  4)  6.9801E+00  2.2683E+00  1.2864E+00 -6.2789E-02
RØW(  5)  9.7829E+00 -1.8540E+00 -3.2278E-01
RØW(  6)  1.9419E+00  1.6469E-01
RØW(  7)  3.9993E+00

ADJ DATA CØRRELATIØN MATRIX
RØW(  1)  1.0000E+00 -4.6468E-01 -4.9153E-01  1.4320E-01  9.6514E-01
-4.2348E-01 -4.2151E-03
RØW(  2)  1.0000E+00  1.3370E-01  5.6074E-01 -3.0360E-01  6.3517E-0
-9.5514E-02
RØW(  3)  1.0000E+00 -1.6838E-01 -4.6294E-01  1.4660E-01  3.9229E-0
RØW(  4)  1.0000E+00  2.7450E-01  3.4941E-01 -1.1884E-02
RØW(  5)  1.0000E+00 -4.2536E-01 -5.1604E-02
RØW(  6)  1.0000E+00  5.9095E-02
RØW(  7)  1.0000E+00
```

RUN 5

```
MULTIPLE REGRESSIØN PRØGRAM

    XMEAN            YMEAN
                 2.363793E+02
 8.224828E+02
 8.373793E+02
 7.915517E+02
 7.732069E+02
-2.238621E+02
-1.233448E+02
-2.900000E+01
```

```
  ØBSERVED          CALCULATED         EST VAR
 1.9100000E+02    1.5428175E+02    2.4877842E+03
 1.4500000E+02    2.5583495E+02    3.0316292E+03
 2.7400000E+02    1.8131787E+02    2.1924171E+03
 2.2800000E+02    1.8444005E+02    3.0953768E+03
 1.5600000E+02    2.6756554E+02    2.8058874E+03
 7.0100000E+02    4.4090838E+02    4.0869005E+03
 9.5000000E+01    2.2602637E+02    5.4963314E+03
 1.3800000E+02    1.9336302E+02    3.4286303E+03
 2.3900000E+02    1.7761720E+02    1.9572336E+03
 1.4500000E+02    1.7333390E+02    2.2289837E+03
 1.1200000E+02    1.7742534E+02    2.8684380E+03
 1.2900000E+02    2.5273370E+02    6.4435959E+03
 1.4900000E+02    1.6767840E+02    2.0865991E+03
 2.2200000E+02    1.7629530E+02    7.0191212E+03
 2.5900000E+02    2.6966915E+02    1.0077516E+03
 1.7300000E+02    2.3298209E+02    2.0812487E+03
 3.3100000E+02    3.1633318E+02    3.1956933E+03
 3.2700000E+02    3.1899459E+02    2.1666915E+03
 3.8800000E+02    1.3324874E+02    3.5990371E+03
 2.2900000E+02    2.2544782E+02    3.8791603E+03
 2.5500000E+02    3.2072278E+02    6.1728024E+03
 2.5700000E+02    2.7093427E+02    4.5704200E+03
 2.2300000E+02    1.9457761E+02    1.9248626E+03
 2.9700000E+02    3.8525164E+02    6.2185045E+03
 3.7400000E+02    2.4131636E+02    1.3317221E+03
 3.5300000E+02    3.4106736E+02    3.2985123E+03
 1.8100000E+02    1.7602357E+02    4.1693351E+03
 1.8200000E+02    2.4347680E+02    2.3717083E+03
 1.0200000E+02    1.5613256E+02    2.8940653E+03
```

RUN 5 (Continued)

```
**************************************************************************
.                   .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
. REGRESSION.          7       .  1.555389E+05  .  2.221985E+04       .
. REMAINDER .         21       .  2.575399E+05  .  1.226381E+04       .
. TOTAL     .         28       .  4.130788E+05  .                     .
**************************************************************************

MULTIPLE CORRELATION COEFFICIENT =  6.136250E-01

CONSTANT TERM(INTERCEPT) =  2.442241E+03


   COEFFICIENTS      EST OF SD
  1.0164109E+00   3.5043322E+00
 -2.4925453E+00   5.0824137E+00
 -2.0713257E+00   1.7772377E+00
  1.1280616E+00   1.5910638E+00
  1.2315423E+00   7.0851822E-01
 -8.7174977E-01   1.2431693E+00
  6.5965652E-01   2.1656701E+00

 F RATIO(  7, 21  DEGREES OF FREEDOM)=  1.811823E+00

 UPPER RT HAND PORTION OF MATRICES ONLY

 INVERSE ADJ DATA MOMENT MATRIX
 ROW(  1)  1.0013E-03 -5.7038E-04  1.9936E-05  1.5617E-04  3.4946E-05
 -5.8283E-05 -6.8153E-05
 ROW(  2)  2.1063E-03 -1.7370E-04 -2.9351E-04 -7.2585E-05  1.3521E-04
  4.6877E-04
 ROW(  3)  2.5755E-04 -1.5066E-04  1.5830E-05 -5.8350E-05  1.8883E-05
 ROW(  4)  2.0642E-04  1.9192E-05 -1.2179E-05 -1.1680E-04
 ROW(  5)  4.0933E-05 -5.3005E-05 -4.2778E-05
 ROW(  6)  1.2602E-04  5.1162E-05
 ROW(  7)  3.8244E-04

 EST COEFFICIENT VAR-COVAR MATRIX
 ROW(  1)  1.2280E+01 -6.9951E+00  2.4449E-01  1.9152E+00  4.2857E-01
 -7.1477E-01 -8.3581E-01
 ROW(  2)  2.5831E+01 -2.1302E+00 -3.5995E+00 -8.9017E-01  1.6582E+00
  5.7489E+00
 ROW(  3)  3.1586E+00 -1.8476E+00  1.9414E-01 -7.1560E-01  2.3158E-01
 ROW(  4)  2.5315E+00  2.3536E-01 -1.4936E-01 -1.4324E+00
 ROW(  5)  5.0200E-01 -6.5004E-01 -5.2462E-01
 ROW(  6)  1.5455E+00  6.2744E-01
 ROW(  7)  4.6901E+00

 ADJ DATA CORRELATION MATRIX
 ROW(  1)  1.0000E+00 -3.9275E-01  3.9257E-02  3.4350E-01  1.7261E-01
 -1.6407E-01 -1.1013E-01
 ROW(  2)  1.0000E+00 -2.3583E-01 -4.4513E-01 -2.4720E-01  2.6244E-01
  5.2230E-01
 ROW(  3)  1.0000E+00 -6.5341E-01  1.5417E-01 -3.2389E-01  6.0168E-02
 ROW(  4)  1.0000E+00  2.0878E-01 -7.5512E-02 -4.1571E-01
 ROW(  5)  1.0000E+00 -7.3800E-01 -3.4190E-01
 ROW(  6)  1.0000E+00  2.3305E-01
 ROW(  7)  1.0000E+00
```

RUN 6

```
MULTIPLE REGRESSION PROGRAM

    XMEAN            YMEAN
                  2.363793E+02
  9.827349E+00
  9.074578E+00
  1.187470E+01
  1.333941E+01
  2.387586E+02
  7.751724E+01
  1.065517E+01
 -1.413793E+00


     OBSERVED           CALCULATED         EST VAR
   1.9100000F+02     1.4357352E+02     5.2650875E+03
   1.4500000E+02     2.5100507E+02     2.9747375E+03
   2.7400000E+02     1.7048439E+02     1.8271849E+03
   2.2800000E+02     1.8943520E+02     3.5001995E+03
   1.5600000E+02     2.8295581E+02     3.7033857E+03
   7.0100000E+02     4.6035979E+02     4.4900138E+03
   9.5000000E+01     1.9938140E+02     6.3367816E+03
   1.3800000E+02     1.8419168E+02     3.9995152E+03
   2.3900000E+02     1.7830961E+02     2.7319487E+03
   1.4500000E+02     1.7628336E+02     1.7780305E+03
   1.1200000E+02     1.7648867E+02     2.5060858E+03
   1.2900000E+02     2.6030870E+02     7.3608817E+03
   1.4900000E+02     1.8120280E+02     3.4371625E+03
   2.2200000E+02     1.7417364E+02     7.0632825E+03
   2.5900000E+02     2.6743936E+02     1.0426012E+03
   1.7300000E+02     2.3688920E+02     2.0657528E+03
   3.3100000E+02     3.1849516E+02     3.3541844E+03
   3.2700000E+02     3.2940746E+02     2.8196238E+03
   3.8800000E+02     1.3771054E+02     3.1960301E+03
   2.2900000E+02     2.2283218E+02     3.6016420E+03
   2.5500000F+02     3.1639798E+02     7.8090645E+03
   2.5700000E+02     2.5733025E+02     6.8128232E+03
   2.2300000E+02     1.9565390E+02     2.0078595E+03
   2.9700000E+02     3.8880613E+02     6.0070475E+03
   3.7400000E+02     2.4979317E+02     1.8984281E+03
   3.5300000E+02     3.3158829E+02     3.3300662E+03
   1.8100000E+02     1.7504447E+02     3.4877042F+03
   1.8200000E+02     2.4823215E+02     2.9347674E+03
   1.0200000E+02     1.5122622E+02     2.8208440E+03
```

RUN 6 (Continued)

```
***************************************************************************
*              .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
* REGRESSION.        8      .  1.682727E+05  .  2.103409E+04      .
* REMAINDER .       20      .  2.448061E+05  .  1.224030E+04      .
* TOTAL     .       28      .  4.130788E+05  .                    .
***************************************************************************

MULTIPLE CORRELATION COEFFICIENT =  6.382494E-01

CONSTANT TERM(INTERCEPT) =  8.747569E+01


  COEFFICIENTS      EST OF SD
  1.6155524E+01   6.5450923E+01
 -1.3149299E+01   1.0449889E+02
  5.6432606E+01   3.7626343E+01
 -2.3488160E+01   2.4915874E+01
 -1.3188585E+00   8.3700842E-01
  9.9253017E-01   1.3187024E+00
 -7.8814243E-01   2.2304178E+00
  7.0144814E-01   2.6216908E+00
```

```
 F RATIO(  8, 20  DEGREES OF FREEDOM)=  1.718429E+00

UPPER RT HAND PORTION OF MATRICES ONLY

INVERSE ADJ DATA MOMENT MATRIX
ROW(  1)  3.4998E-01 -2.0495E-01  8.0006E-03  1.4299E-02 -6.8523E-04
 4.6639E-04 -1.3135E-03  3.8213E-03
ROW(  2)  8.9214E-01 -1.6692E-01  3.9091E-02  5.5051E-04 -7.8406E-04
 8.2054E-03 -1.3965E-03
ROW(  3)  1.1566E-01 -6.5065E-02  5.3671E-04 -3.0573E-04 -4.5553E-03
-1.9209E-03
ROW(  4)  5.0718E-02 -4.5072E-04  5.9846E-04  3.3340E-03  4.5525E-04
ROW(  5)  5.7236E-05 -7.0654E-05 -4.5807E-05 -9.2117E-05
ROW(  6)  1.4207E-04  5.5719E-05  1.0521E-04
ROW(  7)  4.0642E-04 -3.7772E-05
ROW(  8)  5.6153E-04

EST COEFFICIENT VAR-COVAR MATRIX
ROW(  1)  4.2838E+03 -2.5086E+03  9.7930E+01  1.7503E+02 -8.3874E+00
 5.7088E+00 -1.6078E+01  4.6774E+01
ROW(  2)  1.0920E+04 -2.0431E+03  4.7848E+02  6.7384E+00 -9.5971E+00
 1.0044E+02 -1.7094E+01
ROW(  3)  1.4157E+03 -7.9641E+02  6.5695E+00 -3.7422E+00 -5.5758E+01
-2.3512E+01
ROW(  4)  6.2080E+02 -5.5169E+00  7.3253E+00  4.0809E+01  5.5725E+00
ROW(  5)  7.0058E-01 -8.6483E-01 -5.6069E-01 -1.1275E+00
ROW(  6)  1.7390E+00  6.8202E-01  1.2879E+00
ROW(  7)  4.9748E+00 -4.6234E-01
ROW(  8)  6.8733E+00
```

RUN 6 (Continued)

```
ADJ DATA C0RRELATI0N MATRIX
R0W(  1)  1.0000E+00 -3.6678E-01  3.9766E-02  1.0733E-01 -1.5310E-01
 6.6143E-02 -1.1013E-01  2.7259E-01
R0W(  2)  1.0000E+00 -5.1962E-01  1.8377E-01  7.7039E-02 -6.9644E-02
 4.3092E-01 -6.2394E-02
R0W(  3)  1.0000E+00 -8.4951E-01  2.0860E-01 -7.5421E-02 -6.6440E-01
-2.3835E-01
R0W(  4)  1.0000E+00 -2.6454E-01  2.2295E-01  7.3433E-01  8.5308E-02
R0W(  5)  1.0000E+00 -7.8353E-01 -3.0034E-01 -5.1383E-01
R0W(  6)  1.0000E+00  2.3188E-01  3.7251E-01
R0W(  7)  1.0000E+00 -7.9067E-02
R0W(  8)  1.0000E+00
```

ASARCO
Data Set 3
ASAR 3

```
ASAR3         09:37EST     12/02/74

100 131,820,1070,820,850,730,770,690,700
101 139,820,1030,820,880,770,770,735,730
102 24,825,1080,840,920,800,815,795,800
103 48,820,1040,840,910,800,815,745,800
104 51,825,1000,820,860,790,780,750,765
105 156,830,1100,830,900,760,780,755,780
106 95,830,1000,830,860,795,780,740,730
107 30,830,1015,830,870,770,770,750,755,
108 138,830,1070,845,930,805,840,785,775
109 47,825,1045,845,930,825,830,820,815
110 239,825,1120,840,940,800,835,795,810
111 145,820,1075,845,945,835,840,825,815
112 47,820,1030,840,910,815,815,810,810
113 DELETE
114 38,820,1105,840,930,790,800,740,760
115 37,820,1000,835,880,780,800,775,760
116 41,820,1055,845,910,810,820,795,780
118 112,815,1100,850,955,820,850,825,820
119 43,815,990,840,890,820,800,735,800
120 129,830,1000,850,900,790,790,745,750
121 164,804,914,822,852,736,722,684,678
122 43,835,1110,830,865,720,735,720,725
123 60,825,1000,810,840,735,735,720,720
124 27,830,1100,820,855,725,735,725,725
125 100,835,1055,825,850,745,755,730,730
126 100,825,1070,840,915,790,780,760,765
127 43,835,1015,830,860,780,785,765,755
128 222,825,1070,830,955,825,790,770,755
130 259,820,1055,835,915,780,780,760,755
131 128,815,960,835,885,790,780,770,760
133 173,815,1075,835,895,775,800,765,770
134 102,810,1075,845,940,810,800,780,775
135 331,830,1060,830,910,770,790,770,700
136 48,815,980,835,890,790,790,775,770
137 327,830,1010,835,870,765,785,750,765
138 388,830,1110,850,930,800,815,765,770
139 229,810,1000,840,890,825,840,815,800
140 92,815,1070,840,925,800,805,785,795
141 71,830,1070,820,865,750,760,730,730
142 95,820,1070,840,940,810,770,775,765
143 117,820,1070,840,890,825,830,790,785
144 67,820,970,830,855,795,800,790,800
145 105,830,935,835,860,810,805,760,760
147 107,835,1005, 845,885,760,765,740,745
148 60,835,1100,845,950,810,800,765,755
149 33,835,1030,850,900,790,815,790,785
150 48,830,1030,850,900,785,785,760,765
151 223,825,1090,840,895,785,805,770,780
152 107,820,1005,840,890,790,800,785,800
153 48,830,1030,840,890,765,765,735,735
154 202,825,1095,840,955,825,825,785,775
155 102,820,1065,840,920,800,800,780,790
156 146,820,980,830,870,770,775,765,755
157 67,820,1000,835,875,770,775,765,765
158 297,820,1010,835,740,770,780,765,750
159 117,815,1030,840,735,785,790,760,750
160 164,835,1045,840,890,760,775,740,745
161 122,835,1085,850,945,810,815,760,755
162 85,820,1080,840,900,790,815,780,780
163 399,820,1065,835,890,765,750,715,710
164 89,825,1050,850,920,810,800,785,775
165 228,825,1065,840,910,785,775,750,750
166 140,825,1000,845,875,780,785,725,725
167 294,835,1030,825,860,755,790,750,740
168 92,835,955,840,865,780,775,730,725
```

```
                    DESCRIPTIVE STATISTICS FOR Y1

NUMBER OF OBSERVATIONS .......................................... 64

MEAN = XBR = SUM(X(I))/N ................................    127.36

MEDIAN ..................................................    103.50

RANGE ...................................................    375.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................    8126.4

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........    90.138

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........    8257.4

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................    90.870

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............    1.2557

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................    4.0028

                2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
                -----------------------------------------------------------
                          MEAN                      STANDARD DEVIATION
                --------------------------     ----------------------------
CONFIDENCE        LOWER           UPPER           LOWER           UPPER
  LEVEL           LIMIT           LIMIT           LIMIT           LIMIT

  90.0%           108.40          146.32          79.394          106.64
  95.0%           104.66          150.06          77.403          110.05
  99.0%           97.189          157.53          73.748          117.25
                                               FOR A NORMAL DISTRIBUTION
   1         131           24          1.538          12.768          11.229
   2         139           27          3.077          13.470          10.394
   3          24           30          4.615          14.199           9.584
   4          48           33          6.154          14.954           8.800
   5          51           37          7.692          16.002           8.310
   6         156           38          9.231          16.271           7.040
   7          95           41         10.769          17.096           6.327
   8          30           43         15.385          17.661           2.277
   9         138           43         15.385          17.661           2.277
  10          47           43         15.385          17.661           2.277
  11         239           47         18.462          18.826           0.364
  12         145           47         18.462          18.826           0.364
  13          47           48         24.615          19.124          -5.491
  14          38           48         24.615          19.124          -5.491
  15          37           48         24.615          19.124          -5.491
  16          41           48         24.615          19.124          -5.491
  17         112           51         26.154          20.037          -6.117
  18          43           60         29.231          22.927          -6.304
  19         129           60         29.231          22.927          -6.304
  20         164           67         32.308          25.327          -6.981
  21          43           67         32.308          25.327          -6.981
  22          60           71         33.846          26.756          -7.090
  23          27           85         35.385          32.055          -3.329
  24         100           89         36.923          33.646          -3.277
  25         100           92         40.000          34.859          -5.141
  26          43           92         40.000          34.859          -5.141
  27         222           95         43.077          36.088          -6.989
  28         259           95         43.077          36.088          -6.989
  29         128          100         46.154          38.168          -7.986
  30         173          100         46.154          38.168          -7.986
  31         102          102         49.231          39.009         -10.221
  32         331          102         49.231          39.009         -10.221
  33          48          105         50.769          40.282         -10.487
  34         327          107         53.846          41.136         -12.710
  35         388          107         53.846          41.136         -12.710
  36         229          112         55.385          43.289         -12.096
  37          92          117         58.462          45.462         -13.000
  38          71          117         58.462          45.462         -13.000
  39          95          122         60.000          47.648         -12.352
  40         117          128         61.538          50.281         -11.457
  41          67          129         63.077          50.720         -12.357
  42         105          131         64.615          51.598         -13.017
  43         107          138         66.154          54.661         -11.493
  44          60          139         67.692          55.097         -12.596
  45          33          140         69.231          55.532         -13.699
  46          48          145         70.769          57.696         -13.073
  47         223          146         72.308          58.127         -14.181
  48         107          156         73.846          62.369         -11.477
  49          48          164         76.923          65.661         -11.262
  50         202          164         76.923          65.661         -11.262
  51         102          173         78.462          69.226          -9.236
  52         146          202         80.000          79.429          -0.571
  53          67          222         81.538          85.118           3.579
  54         297          223         83.077          85.371           2.294
  55         117          228         84.615          86.597           1.981
  56         164          229         86.154          86.833           0.679
  57         122          239         87.692          89.038           1.346
  58          85          259         89.231          92.628           3.398
  59         399          294         90.769          96.666           5.897
  60          89          297         92.308          96.904           4.596
  61         228          327         93.846          98.599           4.753
  62         140          331         95.385          98.749           3.364
  63         294          388         96.923          99.794           2.871
  64          92          399         98.462          99.860           1.399

        0.1531 = KOLMOGOROV-SMIRNOV STATISTIC
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              DESCRIPTIVE STATISTICS FØR X1

NUMBER ØF ØBSERVATIØNS ..............................................  64

MEAN = XBR = SUM(X(I))/N ................................     824.20

MEDIAN ..................................................     825.00

RANGE ...................................................     31.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................     52.349

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........     7.2353

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........     53.180

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................     7.2925

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............   -0.23593

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     2.5926

                  2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
                  ---------------------------------------------------------
                              MEAN                      STANDARD DEVIATIØN
                  -------------------------       -------------------------
CØNFIDENCE          LØWER             UPPER          LØWER           UPPER
  LEVEL             LIMIT             LIMIT          LIMIT           LIMIT

  90.0%               822.68            825.72          6.3715          8.5584
  95.0%               822.38            826.02          6.2117          8.8321
  99.0%               821.78            826.62          5.9184          9.4098
                                                  FØR A NØRMAL  DISTRIBUTIØN
   1          820          804          1.538          0.280          -1.259
   2          820          810          4.615          2.573          -2.042
   3          825          810          4.615          2.573          -2.042
   4          820          815         15.385         10.347          -5.037
   5          825          815         15.385         10.347          -5.037
   6          830          815         15.385         10.347          -5.037
   7          830          815         15.385         10.347          -5.037
   8          830          815         15.385         10.347          -5.037
   9          830          815         15.385         10.347          -5.037
  10          825          815         15.385         10.347          -5.037
  11          825          820         44.615         28.218         -16.397
  12          820          820         44.615         28.218         -16.397
  13          820          820         44.615         28.218         -16.397
  14          820          820         44.615         28.218         -16.397
  15          820          820         44.615         28.218         -16.397
  16          820          820         44.615         28.218         -16.397
  17          815          820         44.615         28.218         -16.397
  18          815          820         44.615         28.218         -16.397
  19          830          820         44.615         28.218         -16.397
  20          804          820         44.615         28.218         -16.397
  21          835          820         44.615         28.218         -16.397
  22          825          820         44.615         28.218         -16.397
  23          830          820         44.615         28.218         -16.397
  24          835          820         44.615         28.218         -16.397
  25          825          820         44.615         28.218         -16.397
  26          835          820         44.615         28.218         -16.397
  27          825          820         44.615         28.218         -16.397
  28          820          820         44.615         28.218         -16.397
  29          815          820         44.615         28.218         -16.397
  30          815          825         63.077         54.351          -8.726
  31          810          825         63.077         54.351          -8.726
  32          830          825         63.077         54.351          -8.726
  33          815          825         63.077         54.351          -8.726
  34          830          825         63.077         54.351          -8.726
  35          830          825         63.077         54.351          -8.726
  36          810          825         63.077         54.351          -8.726
  37          815          825         63.077         54.351          -8.726
  38          830          825         63.077         54.351          -8.726
  39          820          825         63.077         54.351          -8.726
  40          820          825         63.077         54.351          -8.726
  41          820          825         63.077         54.351          -8.726
  42          830          830         83.077         78.667          -4.410
  43          835          830         83.077         78.667          -4.410
  44          835          830         83.077         78.667          -4.410
  45          835          830         83.077         78.667          -4.410
  46          830          830         83.077         78.667          -4.410
  47          825          830         83.077         78.667          -4.410
  48          820          830         83.077         78.667          -4.410
  49          830          830         83.077         78.667          -4.410
  50          825          830         83.077         78.667          -4.410
  51          820          830         83.077         78.667          -4.410
  52          820          830         83.077         78.667          -4.410
  53          820          830         83.077         78.667          -4.410
  54          820          830         83.077         78.667          -4.410
  55          815          835         98.462         93.064          -5.398
  56          835          835         98.462         93.064          -5.398
  57          835          835         98.462         93.064          -5.398
  58          820          835         98.462         93.064          -5.398
  59          820          835         98.462         93.064          -5.398
  60          825          835         98.462         93.064          -5.398
  61          825          835         98.462         93.064          -5.398
  62          825          835         98.462         93.064          -5.398
  63          835          835         98.462         93.064          -5.398
  64          835          835         98.462         93.064          -5.398

        0.1709 = KØLMØGØRØV-SMIRNØV STATISTIC
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                      DESCRIPTIVE STATISTICS FOR X2

NUMBER OF OBSERVATIONS .......................................... 64

MEAN = XBR = SUM(X(I))/N ...................................... 1040.9

MEDIAN  ....................................................... 1052.5

RANGE   ....................................................... 206.1

UNADJUSTED (BIASED) VARIANCE =
  SUM ((X(I)-XBR)**2)N = UVR   ................................ 2077.2

UNADJUSTED STANDARD DEVIATION = SORT(UVR) = S ................. 45.57

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR .............. 2143.7

ADJUSTED STANDARD DEVIATION = SORT(AVR)........................ 46.31

          2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
          ----------------------------------------------------------
                      MEAN                       STANDARD DEVIATION
          --------------------------          ----------------------

CONFIDENCE      LOWER       UPPER             LOWER           UPPER
  LEVEL         LIMIT       LIMIT             LIMIT           LIMIT

  90.0%         1031.4      1050.4            41.3            55.9
  95.0%         1029.5      1052.3            40.4            57.62
  99.0%         1025.9      1055.9            38.35           61.7

                                      FOR A NORMAL DISTRIBUTION

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                 DESCRIPTIVE STATISTICS FOR X3

NUMBER OF OBSERVATIONS .........................................  64

MEAN = XBR = SUM(X(I))/N ................................     836.75

MEDIAN ..................................................     840.00

RANGE ...................................................     40.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................     78.875

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........     8.8812

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........     80.127

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................     8.9514

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............   -0.67846

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     3.1771

                 2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
                 ---------------------------------------------------------
                            MEAN                       STANDARD DEVIATION
                 ------------------------       ------------------------
CONFIDENCE          LOWER         UPPER            LOWER          UPPER
 LEVEL              LIMIT         LIMIT            LIMIT          LIMIT

 90.0%             834.88        838.62           7.8209         10.505
 95.0%             834.51        838.99           7.6248         10.841
 99.0%             833.78        839.72           7.2647         11.550
                                                FOR A NORMAL DISTRIBUTION


                   *****************************************

              X3
              INPUT        ORDERED       CUMULATIVE     CUMULATIVE
               DATA         DATA         PERCENTAGE      NORMAL       DIFFERENCE

     10       845            830           27.692        22.540         -5.152
     20       822            835           43.077        42.250         -0.827
     30       835            840           75.385        64.172        -11.212
     40       840            840           75.385        64.172        -11.212
     50       840            845           87.692        82.164         -5.528
     60       850            850           98.462        93.059         -5.402

              0.2042 = KOLMOGOROV-SMIRNOV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FØR X4 :

NUMBER ØF ØBSERVATIØNS .........................................   64

MEAN = XBR = SUM(X(I))/N ...................................    891.91

MEDIAN .....................................................    890.00

RANGE ......................................................    220.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR .................................    1689.2

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ..............    41.100

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR............    1716.1

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ....................    41.425

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) .................   -1.3778

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ...................    6.9509

              2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
              ------------------------------------------------------------
                        MEAN                         STANDARD DEVIATIØN
              -----------------------------      -------------------------
CØNFIDENCE       LØWER          UPPER               LØWER          UPPER
 LEVEL           LIMIT          LIMIT               LIMIT          LIMIT

 90.0%           883.26         900.55              36.194         48.616
 95.0%           881.56         902.25              35.286         50.171
 99.0%           878.15         905.66              33.620         53.453
                                                 FØR A NØRMAL DISTRIBUTIØN

                *****************************************

              X4
              INPUT       ØRDERED     CUMULATIVE     CUMULATIVE
               DATA        DATA       PERCENTAGE       NØRMAL      DIFFERENCE

  10          930          860         20.000         22.059         2.059
  20          852          875         32.308         34.159         1.852
  30          895          890         50.769         48.165        -2.604
  40          890          900         61.538         57.745        -3.793
  50          955          920         76.923         75.117        -1.306
  60          920          945         92.308         90.002        -2.306

               0.1090 = KØLMØGØRØV-SMIRNØV STATISTIC
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```
                 DESCRIPTIVE STATISTICS FØR X5

NUMBER ØF ØBSERVATIØNS ............................................  64

MEAN = XBR = SUM(X(I))/N ...................................   785.95

MEDIAN .....................................................   790.00

RANGE ......................................................   115.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR .................................   699.11

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ..............   26.441

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR............   710.20

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ....................   26.650

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) .................  -0.46017

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ...................   2.7862

           2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
           ----------------------------------------------------------
                     MEAN
           -------------------------      STANDARD DEVIATIØN
CØNFIDENCE                               ------------------------
  LEVEL     LØWER         UPPER          LØWER          UPPER
            LIMIT         LIMIT          LIMIT          LIMIT

  90.0%      780.39        791.51         23.284         31.276
  95.0%      779.30        792.61         22.700         32.276
  99.0%      777.10        794.80         21.628         34.387
                                         FØR A NØRMAL DISTRIBUTIØN

            *****************************************

          X5
          INPUT     ØRDERED      CUMULATIVE    CUMULATIVE
          DATA      DATA         PERCENTAGE      NØRMAL      DIFFERENCE
   10     825
   20     736        760          16.923         16.506        -0.417
   30     775        770          30.769         27.471        -3.298
   40     825        785          46.154         48.573         2.420
   50     825        795          63.077         63.287         0.210
   60     810        810          63.077         81.656        -1.421
                     825          96.923         92.857        -4.066

          0.0916 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                    DESCRIPTIVE STATISTICS FØR X6

NUMBER ØF ØBSERVATIØNS ........................................   64

MEAN = XBR = SUM(X(I))/N .............................        791.36

MEDIAN ...............................................        790.00

RANGE ................................................        128.00

INADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ...........................        727.82

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ............    26.978

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR..........    739.38

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ..................    27.191

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ...............  -0.17163

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) .................    3.0185

                  2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
                  -------------------------------------------------------
                               MEAN                     STANDARD DEVIATIØN
                  --------------------------         ------------------------
CØNFIDENCE           LØWER          UPPER              LØWER          UPPER
  LEVEL              LIMIT          LIMIT              LIMIT          LIMIT

  90.07              785.69         797.03             23.757         31.912
  95.07              784.57         798.15             23.162         32.932
  99.07              782.33         800.39             22.068         35.086
                                                 FØR A NØRMAL DISTRIBUTIØN

                    ****************************************


              X6
              INPUT        ØRDERED        CUMULATIVE   CUMULATIVE
               DATA         DATA          PERCENTAGE      NØRMAL     DIFFERENCE

     10       830           770           20.000        21.608        1.608
     20       722           780           38.462        33.806       -4.655
     30       800           790           53.846        48.006       -5.840
     40       830           800           69.231        62.467       -6.764
     50       825           815           84.615        80.769       -3.846
     60       800           835           92.308        94.575        2.267

               0.0785 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
            DESCRIPTIVE STATISTICS FOR X7

NUMBER OF OBSERVATIONS .......................................... 64

MEAN = XBR = SUM(X(I))/N ................................     761.94

MEDIAN ..................................................     765.00

RANGE ...................................................     141.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................     856.03

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........     29.258

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........     869.62

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................     29.489

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............   -0.12111

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     3.1532

            2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
            ---------------------------------------------------------
                      MEAN                      STANDARD DEVIATION
            -------------------------       -------------------------
CONFIDENCE    LOWER        UPPER               LOWER        UPPER
  LEVEL       LIMIT        LIMIT               LIMIT        LIMIT

  90.0%       755.78       768.09              25.765       34.608
  95.0%       754.57       769.30              25.119       35.715
  99.0%       752.15       771.73              23.933       38.051
                                        FOR A NORMAL DISTRIBUTION


               ****************************************


         X7
         INPUT        ORDERED       CUMULATIVE    CUMULATIVE
          DATA         DATA         PERCENTAGE      NORMAL      DIFFERENCE

   10    820           730           15.385        13.940        -1.445
   20    684           750           36.923        34.281        -2.642
   30    765           760           47.692        47.381        -0.312
   40    790           770           64.615        60.773        -3.842
   50    785           785           81.538        78.291        -3.247
   60    785           810           92.308        94.843         2.535

         0.0832 = KOLMOGOROV-SMIRNOV STATISTIC
```

```
                    DESCRIPTIVE STATISTICS FØR X8

NUMBER ØF ØBSERVATIØNS ........................................   64

MEAN = XBR = SUM(X(I))/N ................................      761.92

MEDIAN ..................................................      762.50

RANGE ...................................................      142.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................      920.51

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........      30.340

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........      935.12

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................      30.580

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............    -0.27644

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................      2.8667

                  2-SIDED CONFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
                  ----------------------------------------------------------
                               MEAN                      STANDARD DEVIATIØN
                  ---------------------------       ------------------------
CØNFIDENCE          LØWER          UPPER              LØWER         UPPER
  LEVEL             LIMIT          LIMIT              LIMIT         LIMIT

   90.0%             755.54         768.30              26.718        35.888
   95.0%             754.28         769.56              26.048        37.036
   99.0%             751.77         772.07              24.818        39.458
                                                    FØR A NØRMAL DISTRIBUTIØN

                     ****************************************

                X8
                INPUT        ORDERED       CUMULATIVE     CUMULATIVE
                 DATA         DATA         PERCENTAGE       NØRMAL       DIFFERENCE

      10        815            730           20.000          14.827         -5.173
      20        678            750           32.308          34.832          2.524
      30        770            760           49.231          47.494         -1.736
      40        785            770           63.077          60.417         -2.660
      50        775            785           78.462          77.478         -0.983
      60        775            810           93.846          94.205          0.359

                0.0827 = KOLMØGØRØV-SMIRNØV STATISTIC
```

MULTIPLE REGRESSION ANALYSIS

ASARCO PLANT - START-UP DATA

ASARCO

Data Set

STA 1

```
100 5.0,12.5
101 6.0,51.5
102 5.0,6.5
103 7.0,16.5
104 5.0,9.0
105 9.0,5.5
106 8.0,37
107 6.5,160
108 9.0,16
109 4.0,13.5
110 7.0,16.5
111 6.0,10.5
112 5.0,9.0
```

```
MULTIPLF REGRESSION PROGRAM

    XMEAN          YMEAN
                 6.346154E+00
 2.800000E+01
```

```
  OBSERVED          CALCULATED        EST VAR
5.0000000E+00     6.3005722E+00     2.4523204E-01
6.0000000E+00     6.4152616E+00     2.8661375E-01
5.0000000E+00     6.2829276E+00     2.7467671E-01
7.0000000E+00     6.3123352E+00     2.3090760E-01
5.0000000E+00     6.2902795E+00     2.6124755E-01
9.0000000E+00     6.2799869E+00     2.8051260E-01
8.0000000E+00     6.3726206E+00     2.2411012E-01
6.5000000E+00     6.7343335E+00     2.5243762E+00
9.0000000E+00     6.3108648E+00     2.3246604E-01
4.0000000E+00     6.3035129E+00     2.4125303E-01
7.0000000E+00     6.3123352E+00     2.3090760E-01
6.0000000E+00     6.2946907E+00     2.5398586E-01
5.0000000E+00     6.2902795E+00     2.6124755E-01
```

```
.................................................................
.              .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
. REGRESSION.         1       .  1.808564E-01  .  1.808564E-01     .
. REMAINDER .        11       .  3.051145E+01  .  2.773768E+00     .
. TOTAL     .        12       .  3.069231E+01  .                   .
.................................................................

MULTIPLE CORRELATION COEFFICIENT =  7.676304E-02

CONSTANT TERM(INTERCEPT) =  6.263813E+00


    COEFFICIENTS     EST OF SD
   2.9407546E-03   1.1516670E-02


 F RATIO(  1, 11  DEGREES OF FREEDOM)=  6.520242E-02

 UPPER RT HAND PORTION OF MATRICES ONLY

 INVERSE ADJ DATA MOMENT MATRIX
 ROW(  1)  4.7617E-05

 EST COEFFICIENT VAR-COVAR MATRIX
 ROW(  1)  1.3263E-04

 ADJ DATA CORRELATION MATRIX
 ROW(  1)  1.0000E+00


                 DESCRIPTIVE STATISTICS FOR Y1


NUMBER OF OBSERVATIONS ....................................  13

MEAN = XBR = SUM(X(I))/N ..........................    6.3462

MEDIAN ............................................    6.0000

RANGE .............................................    5.0000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ........................    2.3609

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S .....    1.5365

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR...    2.5577

ADJUSTED STANDARD DEVIATION = SQRT(AVR) ...........    1.5993

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ........   0.41800

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..........    2.0771
```

```
      2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
      ---------------------------------------------------------
                     MEAN                       STANDARD DEVIATIØN
      ---------------------------         -------------------------
CØNFIDENCE   LØWER         UPPER             LØWER        UPPER
  LEVEL      LIMIT         LIMIT             LIMIT        LIMIT

  90.0%        5.5556        7.1367            1.2082       2.4234
  95.0%        5.3797        7.3126            1.1468       2.6400
  99.0%        4.9913        7.7010            1.0414       3.1599
                                          FØR A NØRMAL DISTRIBUTIØN

        ******************************************

          Y1
          INPUT       ØRDERED      CUMULATIVE   CUMULATIVE
          DATA        DATA         PERCENTAGE     NØRMAL     DIFFERENCE

   1      5.0000       4.0000        7.143         7.119       -0.024
   2      6.0000       5.0000       35.714        19.997      -15.717
   3      5.0000       5.0000       35.714        19.997      -15.717
   4      7.0000       5.0000       35.714        19.997      -15.717
   5      5.0000       5.0000       35.714        19.997      -15.717
   6      9.0000       6.0000       50.000        41.432       -8.568
   7      8.0000       6.0000       50.000        41.432       -8.568
   8      6.5000       6.5000       57.143        53.832       -3.311
   9      9.0000       7.0000       71.429        65.867       -5.561
  10      4.0000       7.0000       71.429        65.867       -5.561
  11      7.0000       8.0000       78.571        84.946        6.375
  12      6.0000       9.0000       92.857        95.148        2.291
  13      5.0000       9.0000       92.857        95.148        2.291

          0.1846 = KØLMØGØRØV-SMIRNØV STATISTIC

            DESCRIPTIVE STATISTICS FØR X1


NUMBER ØF ØBSERVATIONS ...........................................  13

MEAN = XBR = SUM(X(I))/N ................................       28.000

MEDIAN ..................................................       13.500

RANGE ...................................................       154.50

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................       1608.7

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........       40.109

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........       1742.7

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................       41.746

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............       2.6964

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................       9.0626
```

```
              2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
              ---------------------------------------------------------
                         MEAN                          STANDARD DEVIATION
              -------------------------          -------------------------
CONFIDENCE       LOWER          UPPER               LOWER          UPPER
  LEVEL          LIMIT          LIMIT               LIMIT          LIMIT

  90.0%          7.3641         48.636              31.538         63.259
  95.0%          2.7730         53.227              29.936         68.912
  99.0%         -7.3665         63.366              27.184         82.484
                                                 FOR A NORMAL DISTRIBUTION


                ****************************************


             X1
             INPUT          ORDERED        CUMULATIVE     CUMULATIVE
              DATA           DATA          PERCENTAGE       NORMAL       DIFFERENCE

    1        12.500         5.5000           7.143          29.495         22.353
    2        51.500         6.5000          14.286          30.327         16.041
    3        6.5000         9.0000          28.571          32.451          3.879
    4        16.500         9.0000          28.571          32.451          3.879
    5        9.0000         10.500          35.714          33.754         -1.961
    6        5.5000         12.500          42.857          35.521         -7.336
    7        37.000         13.500          50.000          36.417        -13.583
    8        160.00         16.000          57.143          38.688        -18.455
    9        16.000         16.500          71.429          39.148        -32.281
   10        13.500         16.500          71.429          39.148        -32.281
   11        16.500         37.000          78.571          58.535        -20.037
   12        10.500         51.500          85.714          71.326        -14.389
   13        9.0000         160.00          92.857          99.922          7.065

             0.3778 = KOLMOGOROV-SMIRNOV STATISTIC
```

ASARCO

Data Set

ASAR2

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```
ASAR2         09:51EST     11/27/74

100 859,820,1120,850,950,835,860,800,780
101 2463,835,1010,830,870,790,780,760,765
102 2145,816,824,770,772,704,710,674,664
103 1863,666,822,720,754,684,692,638,640
104 1695,825,1030,830,875,765,775,745,740
105 1311,830,1075,825,870,745,740,700,695
106 1177,830,1030,845,920,790,765,735,725
107 1012,840,1055,790,750,615,625,700,820
108 3107,810,1030,780,755,635,640,640,645
109 3092,825,980,800,820,700,690,650,640
110 995,835,1065,840,890,765,755,710,710,
111 1088,860,1090,830,845,725,715,690,685
112 1009,810,955,840,860,770,730,685,680
```

```
                  DESCRIPTIVE STATISTICS FØR Y1

NUMBER ØF ØBSERVATIØNS .......................................  13

MEAN = XBR = SUM(X(I))/N ................................     1678.2

MEDIAN ..................................................     1311.0

RANGE ...................................................     2248.0

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR .............................. 0.59019E+06

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........     768.24

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR......... 0.63937E+06

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................     799.61

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............    0.76180

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     2.1775
```

```
                 2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
                 ----------------------------------------------------------
                           MEAN                            STANDARD DEVIATION
                 -----------------------              ---------------------
CONFIDENCE       LOWER         UPPER                  LOWER             UPPER
  LEVEL          LIMIT         LIMIT                  LIMIT             LIMIT

  90.0%             1282.9        2073.4                 604.07            1211.7
  95.0%             1195.0        2161.4                 573.39            1319.9
  99.0%             1000.7        2355.6                 520.69            1579.9
                                                 FOR A NORMAL DISTRIBUTION


                   ****************************************


               Y1
               INPUT          ORDERED        CUMULATIVE     CUMULATIVE
                DATA           DATA          PERCENTAGE       NORMAL       DIFFERENCE

    1           859             859             7.143          15.281          8.138
    2          2463             995            14.286          19.645          5.359
    3          2145            1009            21.429          20.134         -1.295
    4          1863            1012            28.571          20.239         -8.332
    5          1695            1088            35.714          23.024        -12.690
    6          1311            1177            42.857          26.541        -16.316
    7          1177            1311            50.000          32.306        -17.694
    8          1012            1695            57.143          50.840         -6.302
    9          3107            1863            64.286          59.141         -5.145
   10          3092            2145            71.429          72.034          0.606
   11           995            2463            78.571          83.684          5.112
   12          1088            3092            85.714          96.148         10.434
   13          1009            3107            92.857          96.303          3.[illegible]

              0.2154 = KOLMOGOROV-SMIRNOV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FØR X1

NUMBER ØF ØBSERVATIØNS ..........................................  13

MEAN = XBR = SUM(X(I))/N ..............................         815.54

MEDIAN ................................................         825.00

RANGE .................................................         194.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ............................         2028.7

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S .........         45.041

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.......         2197.8

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ...............         46.880

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ............        -2.7100

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..............         9.4331

              2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
              ---------------------------------------------------------
                        MEAN                         STANDARD DEVIATIØN
              --------------------------        -------------------------
CØNFIDENCE      LØWER          UPPER               LØWER         UPPER
  LEVEL         LIMIT          LIMIT               LIMIT         LIMIT

  90.0%          792.36         838.71              35.416        71.039
  95.0%          787.21         843.87              33.617        77.387
  99.0%          775.82         855.25              30.528        92.628
                                               FØR A NØRMAL DISTRIBUTIØN

                ****************************************

             X1
             INPUT        ØRDERED       CUMULATIVE    CUMULATIVE
              DATA         DATA         PERCENTAGE      NØRMAL      DIFFERENCE

     1       820           666            7.143         0.071        -7.072
     2       835           810           21.429        45.298        23.869
     3       816           810           21.429        45.298        23.869
     4       666           816           28.571        50.393        21.821
     5       825           820           35.714        53.791        18.077
     6       830           825           50.000        57.997         7.997
     7       830           825           50.000        57.997         7.997
     8       840           830           64.286        62.114        -2.172
     9       810           830           64.286        62.114        -2.172
    10       825           835           78.571        66.098       -12.474
    11       835           835           78.571        66.098       -12.474
    12       860           840           85.714        69.909       -15.805
    13       810           860           92.857        82.854       -10.003

          0.3761 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
             DESCRIPTIVE STATISTICS FØR X2

NUMBER ØF ØBSERVATIØNS .......................................... 13

MEAN = XBR = SUM(X(I))/N ..............................         1006.6

MEDIAN ................................................         1030.0

RANGE .................................................         298.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ............................         7899.3

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S .........         88.878

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.......         8557.6

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ...............         92.507

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ............        -1.0771

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..............         3.1248

             2-SIDED CONFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
             ----------------------------------------------------------
                        MEAN                         STANDARD DEVIATIØN
             ---------------------------         ----------------------
CØNFIDENCE      LØWER         UPPER               LØWER        UPPER
  LEVEL         LIMIT         LIMIT               LIMIT        LIMIT

  90.0%         960.89        1052.3              69.886       140.18
  95.0%         950.71        1062.5              66.336       152.70
  99.0%         928.25        1085.0              60.239       182.78
                                            FØR A NØRMAL DISTRIBUTIØN


              ******************************************


           X2
          INPUT       ØRDERED      CUMULATIVE    CUMULATIVE
           DATA        DATA        PERCENTAGE      NØRMAL      DIFFERENCE

   1       1120         822           7.143         2.298        -4.844
   2       1010         824          14.286         2.419       -11.867
   3        824         955          21.429        28.844         7.415
   4        822         980          28.571        38.678        10.107
   5       1030        1010          35.714        51.459        15.745
   6       1075        1030          57.143        59.978         2.835
   7       1030        1030          57.143        59.978         2.835
   8       1055        1030          57.143        59.978         2.835
   9       1030        1055          64.286        69.953         5.667
  10        980        1065          71.429        73.602         2.174
  11       1065        1075          78.571        77.012        -1.560
  12       1090        1090          85.714        81.631        -4.083
  13        955        1120          92.857        88.984        -3.873

          0.2152 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FØR X3

NUMBER ØF ØBSERVATIØNS .........................................  13

MEAN = XBR = SUM(X(I))/N ................................      811.54

MEDIAN ..................................................      830.00

RANGE ...................................................      130.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................      1316.9

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........      36.289

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........      1426.6

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................      37.770

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............     -1.1587

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................      3.5286

               2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
               --------------------------------------------------------
                          MEAN                       STANDARD DEVIATIØN
               --------------------------      ------------------------
CØNFIDENCE       LØWER        UPPER              LØWER         UPPER
  LEVEL          LIMIT        LIMIT              LIMIT         LIMIT

  90.0%          792.87       830.21             28.534        57.234
  95.0%          788.71       834.36             27.085        62.349
  99.0%          779.54       843.54             24.595        74.628
                                              FØR A NØRMAL DISTRIBUTIØN


                  ****************************************


           X3
           INPUT        ØRDERED        CUMULATIVE    CUMULATIVE
            DATA         DATA          PERCENTAGE      NØRMAL      DIFFERENCE

    1      850           720             7.143          0.768        -6.374
    2      830           770            14.286         13.572        -0.714
    3      770           780            21.429         20.186        -1.243
    4      720           790            28.571         28.426        -0.146
    5      830           800            35.714         38.000         2.285
    6      825           825            42.857         63.923        21.066
    7      845           830            64.286         68.750         4.465
    8      790           830            64.286         68.750         4.465
    9      780           830            64.286         68.750         4.465
   10      800           840            78.571         77.444        -1.128
   11      840           840            78.571         77.444        -1.128
   12      830           845            85.714         81.217        -4.497
   13      840           850            92.857         84.573        -8.284

          0.2546 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                    DESCRIPTIVE STATISTICS FØR X4

NUMBER ØF ØBSERVATIØNS ........................................   13

MEAN = XBR = SUM(X(I))/N ................................     840.85

MEDIAN ..................................................     860.00

RANGE ...................................................     200.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................     4014.3

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........     63.358

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........     4348.8

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................     65.945

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............   -0.10921

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     1.8710

                 2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
                 ---------------------------------------------------------
                          MEAN                       STANDARD DEVIATIØN
                 -------------------------        ----------------------
CØNFIDENCE       LØWER         UPPER              LØWER         UPPER
  LEVEL          LIMIT         LIMIT              LIMIT         LIMIT

  90.0%            808.25        873.44            49.819        99.929
  95.0%            801.00        880.70            47.289        108.86
  99.0%            784.98        896.71            42.942        130.30
                                                  FØR A NØRMAL DISTRIBUTIØN


                  ****************************************


             X4
            INPUT       ØRDERED      CUMULATIVE   CUMULATIVE
             DATA        DATA        PERCENTAGE     NØRMAL      DIFFERENCE

     1      950          750            7.143        8.416         1.274
     2      870          754           14.286        9.393        -4.893
     3      772          755           21.429        9.650       -11.779
     4      754          772           28.571       14.825       -13.747
     5      875          820           35.714       37.596         1.882
     6      870          845           42.857       52.511         9.654
     7      920          860           50.000       61.426        11.426
     8      750          870           64.286       67.079         2.793
     9      755          870           64.286       67.079         2.793
    10      820          875           71.429       69.774        -1.655
    11      890          890           78.571       77.198        -1.374
    12      845          920           85.714       88.499         2.784
    13      860          950           92.857       95.106         2.249

             0.1594 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
               DESCRIPTIVE STATISTICS FOR X5

NUMBER OF OBSERVATIONS .....................................      13

MEAN = XBR = SUM(X(I))/N ..............................       732.54

MEDIAN ................................................       745.00

RANGE .................................................       220.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ............................       3721.8

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S .........       61.006

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.......       4031.9

ADJUSTED STANDARD DEVIATION = SQRT(AVR) ...............       63.498

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ............     -0.38832

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..............       2.3599

             2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
             ---------------------------------------------------------
                        MEAN                       STANDARD DEVIATION
             --------------------------         -------------------------
CONFIDENCE     LOWER        UPPER                LOWER         UPPER
  LEVEL        LIMIT        LIMIT                LIMIT         LIMIT

  90.0%          701.15       763.93               47.970        96.219
  95.0%          694.17       770.91               45.533        104.82
  99.0%          678.74       786.33               41.348        125.46
                                                FOR A NORMAL DISTRIBUTION


               ***************************************


          X5
          INPUT        ORDERED        CUMULATIVE     CUMULATIVE
           DATA         DATA          PERCENTAGE       NORMAL        DIFFERENCE

    1     835            615            7.143          3.208          -3.935
    2     790            635           14.286          6.226          -8.060
    3     704            684           21.429         22.231           0.802
    4     684            700           28.571         30.417           1.846
    5     765            704           35.714         32.656          -3.059
    6     745            725           42.857         45.275           2.418
    7     790            745           50.000         57.779           7.779
    8     615            765           64.286         69.540           5.255
    9     635            765           64.286         69.540           5.255
   10     700            770           71.429         72.239           0.811
   11     765            790           85.714         81.725          -3.989
   12     725            790           85.714         81.725          -3.989
   13     770            835           92.857         94.670           1.812

          0.1569 = KOLMOGOROV-SMIRNOV STATISTIC
```

```
                  DESCRIPTIVE STATISTICS FØR X6

NUMBER ØF ØBSERVATIØNS ..........................................  13

MEAN = XBR = SUM(X(I))/N ..............................       729.00

MEDIAN ................................................       730.00

RANGE .................................................       235.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ............................       3550.5

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S .........       59.586

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.......       3846.3

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ...............       62.019

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ............      0.21607

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..............       3.0022

                 2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
                 ------------------------------------------------------------
                             MEAN                         STANDARD DEVIATIØN
                 ---------------------------          -------------------------
CØNFIDENCE          LØWER         UPPER                  LØWER          UPPER
  LEVEL             LIMIT         LIMIT                  LIMIT          LIMIT

  90.0%            698.34        759.66                 46.853         93.978
  95.0%            691.52        766.48                 44.473         102.38
  99.0%            676.46        781.54                 40.385         122.54
                                                      FØR A NØRMAL DISTRIBUTIØN


                  *****************************************


                X6
                INPUT        ØRDERED       CUMULATIVE    CUMULATIVE
                 DATA         DATA         PERCENTAGE      NØRMAL      DIFFERENCE

        1       860           625             7.143         4.678        -2.465
        2       780           640            14.286         7.564        -6.722
        3       710           690            21.429        26.473         5.044
        4       692           692            28.571        27.539        -1.032
        5       775           710            35.714        37.967         2.252
        6       740           715            42.857        41.070        -1.787
        7       765           730            50.000        50.643         0.643
        8       625           740            57.143        57.039        -0.104
        9       640           755            64.286        66.248         1.962
       10       690           765            71.429        71.920         0.492
       11       755           775            78.571        77.087        -1.485
       12       715           780            85.714        79.456        -6.259
       13       730           860            92.857        98.267         5.410

                0.1285 = KØLMØGØRØV-SMIRNØV STATISTIC
                DESCRIPTIVE STATISTICS FØR X7

NUMBER ØF ØBSERVATIØNS ........................................  13

MEAN = XBR = SUM(X(I))/N ................................    702.08

MEDIAN ..................................................    700.00

RANGE ...................................................    162.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................    2141.5

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........    46.276

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........    2319.9

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................    48.165

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............   0.44723

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................    2.4753

                2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
                -----------------------------------------------------------
                           MEAN                     STANDARD DEVIATIØN
                -------------------------        -------------------------
CØNFIDENCE          LØWER         UPPER              LØWER         UPPER
  LEVEL             LIMIT         LIMIT              LIMIT         LIMIT

  90.0%            678.27        725.89             36.387        72.986
  95.0%            672.97        731.18             34.539        79.508
  99.0%            661.27        742.88             31.364        95.167
                                              FØR A NØRMAL DISTRIBUTIØN


                  ****************************************


             X7
           INPUT        ØRDERED      CUMULATIVE     CUMULATIVE
            DATA          DATA       PERCENTAGE       NØRMAL       DIFFERENCE

     1      800           638           7.143          9.170          2.027
     2      760           640          14.286          9.873         -4.413
     3      674           650          21.429         13.980         -7.448
     4      638           674          28.571         27.997         -0.574
     5      745           685          35.714         36.146          0.432
     6      700           690          42.857         40.101         -2.756
     7      735           700          57.143         48.280         -8.863
     8      700           700          57.143         48.280         -8.863
     9      640           710          64.286         56.533         -7.753
    10      650           735          71.429         75.287          3.858
    11      710           745          78.571         81.358          2.786
    12      690           760          85.714         88.543          2.829
    13      685           800          92.857         97.898          5.041

          0.1326 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
               DESCRIPTIVE STATISTICS FOR X8

NUMBER OF OBSERVATIONS ............................................  13

MEAN = XBR = SUM(X(I))/N ................................        706.85

MEDIAN ..................................................        695.00

RANGE ...................................................        180.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................        2993.2

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........        54.710

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........        3242.6

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................        56.944

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............       0.53332

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................        2.2669

             2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
             ---------------------------------------------------------
                          MEAN                      STANDARD DEVIATION
             ------------------------          ------------------------
CONFIDENCE      LOWER        UPPER                LOWER         UPPER
  LEVEL         LIMIT        LIMIT                LIMIT         LIMIT

  90.0%           678.70       734.99               43.019        86.289
  95.0%           672.44       741.26               40.834        94.000
  99.0%           658.60       755.09               37.081        112.51
                                               FOR A NORMAL DISTRIBUTION


               ****************************************


            X8
            INPUT        ORDERED       CUMULATIVE    CUMULATIVE
             DATA         DATA         PERCENTAGE      NORMAL      DIFFERENCE

    1       780           640            14.286        12.022        -2.264
    2       765           640            14.286        12.022        -2.264
    3       664           645            21.429        13.872        -7.556
    4       640           664            28.571        22.590        -5.982
    5       740           680            35.714        31.866        -3.848
    6       695           685            42.857        35.062        -7.795
    7       725           695            50.000        41.760        -8.240
    8       820           710            57.143        52.208        -4.934
    9       645           725            64.286        62.506        -1.780
   10       640           740            71.429        71.979         0.550
   11       710           765            78.571        84.643         6.072
   12       685           780            85.714        90.054         4.340
   13       680           820            92.857        97.654         4.797

            0.1209 = KOLMOGOROV-SMIRNOV STATISTIC
```

MULTIPLE REGRESSION ANALYSIS
TEXAS GULF PLANT NORMAL OPERATION

Texas Gulf
Data Set
TGX2

```
TGX2          13:27EST     11/18/74

100 135,806,1118,845,991,821,863,821,846
101 120,805,1115,846,992,822,863,822,846
102 134,806,1118,845,992,821,863,821,846
103 132,800,1118,843,994,822,865,820,847
104 140,803,1113,845,988,816,859,815,842
105 135,803,1117,840,991,818,860,818,842
106 222,797,1104,830,1001,832,886,834,866
107 188,795,1098,828,1001,829,884,832,863
108 200,795,1097,826,1000,826,883,830,862
109 120,806,1125,849,984,811,849,823,850
110 127,803,1117,843,982,808,848,820,849
111 130,805,1120,845,981,808,845,818,848
112 140,808,1128,848,980,800,830,810,838
113 141,811,1134,855,983,808,842,821,847
114 127,809,1130,853,986,813,851,827,851
115 100,799,1121,842,979,816,852,826,849
116 425,805,1110,840,920,730,730,735,755
117 125,799,1120,830,950,763,763,769,786
118 132,801,1128,840,968,790,808,795,822
119 120,803,1125,840,969,800,830,801,830
120 110 ,808,1130,841,970,800,830,803,831
121 70,802,1103,842,977,811,846,801,828
122 80,800,1091,839,975,811,845,805,827
123 60,778,1103,828,960,804,834,806,819
124 118,805,1109,846,999,826,869,821,849
125 110,806,1113,849,999,826,868,821,846
126 110,809,1117,850,999,826,867,821,846
127 200,793,1126,791,791,800,812,793,821
128 130,800,1120,848,980,803,815,818,837
129 95,798,1118,847,983,817,848,833,850
130 100,803,1128,834,972,814,850,830,855
```

RUN 1

```
MULTIPLE REGRESSION PROGRAM

    XMEAN           YMEAN
                 1.379355E+02
  8.019677E+02
  1.116581E+03
  8.409032E+02
  9.753871E+02
  8.094194E+02
  8.438064E+02
  8.132258E+02
  8.385161E+02


   OBSERVED          CALCULATED         EST VAR
 1.3500000E+02     1.2078900E+02     1.7629593E+02
 1.2000000E+02     1.1261185E+02     1.7216112E+02
 1.3400000E+02     1.2078900E+02     1.7629593E+02
 1.3200000E+02     1.0160772E+02     2.1430334E+02
 1.4000000E+02     1.1758125E+02     1.5935394E+02
 1.3500000E+02     1.2855834E+02     1.2542261E+02
 2.2200000E+02     1.1150338E+02     2.8636440E+02
 1.8800000E+02     1.1500999E+02     3.1667466E+02
 2.0000000E+02     1.2596205E+02     3.3377359E+02
 1.2000000E+02     1.3082470E+02     2.2583242E+02
 1.2700000E+02     1.4138118E+02     2.0372619E+02
 1.3000000E+02     1.4250045E+02     1.6594186E+02
 1.4000000E+02     1.5864544E+02     2.2959603E+02
 1.4100000E+02     1.3809330E+02     3.7531740E+02
 1.2700000E+02     1.2826169E+02     3.5310062E+02
 1.0000000E+02     1.1518727E+02     2.0482986E+02
 4.2500000E+02     2.8460406E+02     1.5403200E+03
 1.2500000E+02     1.7975210E+02     7.7819038E+02
 1.3200000E+02     1.6967646E+02     1.7183188E+02
 1.2000000E+02     1.5894531E+02     1.3067693E+02
 1.1000000E+02     1.7552371E+02     2.4079640E+02
 7.0000000E+01     1.2717273E+02     4.5954791E+02
 8.0000000E+01     1.2959251E+02     2.6824281E+02
 6.0000000E+01     9.3029634E+01     1.6558976E+03
 1.1800000E+02     1.0406296E+02     3.0912896E+02
 1.1000000E+02     9.9424274E+01     3.5481437E+02
 1.1000000E+02     1.0780532E+02     4.1230586E+02
 2.0000000E+02     2.5526015E+02     1.9507907E+03
 1.3000000E+02     1.2574157E+02     3.4419073E+02
 9.5000000E+01     9.8117317E+01     4.7251964E+02
 1.0000000E+02     1.5796558E+02     5.5681231E+02
```

RUN 1 (Continued)

```
..............................................................................
.                .DEGREE ØF FREE.   SUM ØF SQUARES. VARIANCE ESTIMATE .
. REGRESSIØN.          4       .   5.330958E+04   .  1.332740E 04      .
. REMAINDER  .        26       .   6.949829E+04   .  2.673011E+03      .
. TØTAL      .        30       .   1.228079E+05   .                    .
..............................................................................

MULTIPLE CØRRELATIØN CØEFFICIENT =  6.588545E-01

CØNSTANT TERM(INTERCEPT) =  8.442381E+02


   CØEFFICIENTS     EST ØF SD
  3.7227268E+00   1.9468376E+00
 -2.7871378E+00   1.0914522E+00
 -2.0432343E+00   1.3717363E+00
  3.7595600E-01   1.3798760E+00


 F RATIØ(  4, 26  DEGREES ØF FREEDØM)=  4.985911E+00

UPPER RT HAND PØRTIØN ØF MATRICES ØNLY

INVERSE ADJ DATA MØMENT MATRIX
RØW(  1)  1.4179E-03 -4.9918E-04 -9.6133E-05  1.0495E-04
RØW(  2)  4.4567E-04  1.6484E-04 -1.7670E-04
RØW(  3)  7.0395E-04 -6.6529E-04
RØW(  4)  7.1233E-04

EST CØEFFICIENT VAR-CØVAR MATRIX
RØW(  1)  3.7902E+00 -1.3343E+00 -2.5697E-01  2.8052E-01
RØW(  2)  1.1913E+00  4.4061E-01 -4.7233E-01
RØW(  3)  1.8817E+00 -1.7783E+00
RØW(  4)  1.9041E+00

ADJ DATA CØRRELATIØN MATRIX
RØW(  1)  1.0000E+00 -6.2795E-01 -9.6222E-02  1.0442E-01
RØW(  2)  1.0000E+00  2.9429E-01 -3.1362E-01
RØW(  3)  1.0000E+00 -9.3950E-01       .
RØW(  4)  1.0000E+00
```

RUN 2

```
MULTIPLE REGRESSION PROGRAM

    XMEAN           YMEAN
                 1.379355E+02
 8.019677E+02
 1.116581E+03
 8.409032E+02
 9.753871E+02
 8.094194E+02
 8.438064E+02
 8.132258E+02
 8.385161E+02


    OBSERVED          CALCULATED        EST VAR
 1.3500000E+02     1.2065665E+02     1.9785551E+02
 1.0000000E+02     1.1030086E+02     1.7332858E+02
 1.3400000E+02     1.2104080E+02     2.0352449E+02
 1.3200000E+02     8.2513986E+01     3.1108493E+02
 1.4000000E+02     1.2426820E+02     2.2289126E+02
 1.3500000E+02     1.3865016E+02     3.8737159E+02
 2.2200000E+02     1.4953898E+02     3.8840641E+02
 1.8800000E+02     1.7398691E+02     4.7998175E+02
 2.0000000E+02     2.0185824E+02     6.1076563E+02
 1.2000000E+02     1.2962520E+02     2.9235762E+02
 1.2700000E+02     1.6646784E+02     3.6230898E+02
 1.3000000E+02     1.5110239E+02     3.4323903E+02
 1.4000000E+02     1.5410184E+02     2.0027279E+02
 1.4100000E+02     1.2018286E+02     3.8303051E+02
 1.2700000E+02     1.2256832E+02     4.0878623E+02
 1.0000000E+02     1.0040894E+02     1.6786530E+02
 4.2500000E+02     3.5849109E+02     1.4481389E+03
 1.2500000E+02     1.4777413E+02     6.1707298E+02
 1.3200000E+02     1.3669044E+02     6.5819022E+02
 1.2000000E+02     1.4210728E+02     3.3319494E+02
 1.1000000E+02     1.6760295E+02     3.9892946E+02
 7.0000000E+01     1.2736958E+02     4.2868723E+02
 8.0000000E+01     1.6318821E+02     7.1413875E+02
 6.0000000E+01     7.8306632E+01     1.3948242E+03
 1.1800000E+02     1.0051801E+02     2.6847986E+02
 1.1000000E+02     8.6469852E+01     2.6215510E+02
 1.1000000E+02     9.1848912E+01     3.5800741E+02
 2.0000000E+02     1.8325247E+02     1.7648602E+03
 1.3000000E+02     7.8800663E+01     1.1139235E+03
 9.5000000E+01     7.9503340E+01     5.6266279E+02
 1.0000000E+02     1.6680497E+02     6.9734915E+02
```

RUN 2 (Continued)

```
     ..............................................................
     .             .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
     . REGRESSION.        8      .  8.332108E+04  .  1.041514E+04     .
     . REMAINDER .       22      .  3.948679E+04  .  1.794854E+03     .
     . TOTAL     .       30      .  1.228079E+05  .                   .
     ..............................................................

MULTIPLE CORRELATION COEFFICIENT =  8.236911E-01

CONSTANT TERM(INTERCEPT) =  3.377379E+03


    COEFFICIENTS     EST OF SD
    6.9265897E+00   2.9622758E+00
   -1.9615544E+00   1.3438454E+00
   -4.9321602E+00   2.6892745E+00
    3.8414428E-01   7.8405521E-01
   -8.0901479E+00   2.8653007E+00
    2.6223307E+00   1.9660347E+00
    3.3243019E+00   3.6216309E+00
   -1.4300937E+00   3.4853787E+00
```

RUN 3

```
  ØBSERVED          CALCULATED        EST VAR
1.3500000E+02     1.2020103E+02     1.9600022E+02
1.2000000E+02     1.1019730E+02     1.7226513E+02
1.3400000E+02     1.2063533E+02     2.0134636E+02
1.3200000E+02     8.2685916E+01     2.8238817E+02
1.4000000E+02     1.2360301E+02     2.1576395E+02
1.3500000E+02     1.3945266E+02     3.9460361E+02
2.2200000E+02     1.5329643E+02     3.8050038E+02
1.8800000E+02     1.7854978E+02     4.8585695E+02
2.0000000E+02     1.9066319E+02     5.6866451E+02
1.2000000E+02     1.2883658E+02     2.8990100E+02
1.2700000E+02     1.6709222E+02     3.7909062E+02
1.3000000E+02     1.5101917E+02     3.5555361E+02
1.4000000E+02     1.5333083E+02     2.0519385E+02
1.4100000E+02     1.1790353E+02     3.6860193E+02
1.2700000E+02     1.2097887E+02     3.9176983E+02
1.0000000E+02     1.0182105E+02     1.7098269E+02
4.2500000E+02     3.6049421E+02     1.4479093E+03
1.2500000E+02     1.4720183E+02     6.1584507E+02
1.3200000E+02     1.3748979E+02     6.4252438E+02
1.2000000E+02     1.4178868E+02     3.2926337E+02
1.1000000E+02     1.6679512E+02     3.9416342E+02
7.0000000E+01     1.2717058E+02     4.2381024E+02
8.0000000E+01     1.6560886E+02     6.9543617E+02
6.0000000E+01     7.6136909E+01     1.3874716E+03
1.1800000E+02     1.0048923E+02     2.7134381E+02
1.1000000E+02     8.5780434E+01     2.6150071E+02
1.1000000E+02     9.0594877E+01     3.5628143E+02
2.0000000E+02     1.8387648E+02     1.7540974E+03
1.3000000E+02     8.1264380E+01     1.1005696E+03
9.5000000E+01     8.1622675E+01     5.7953856E+02
1.0000000E+02     1.6949627E+02     6.9552187E+02
```

RUN 3 (Continued)

```
...............................................................
.               .DEGREE OF FREE.  SUM OF SQUARES. VARIANCE ESTIMATE .
. REGRESSION.           8       .  8.366312E+04  .  1.045789E+04    .
. REMAINDER .          22       .  3.914475E+04  .  1.779307E+03    .
. TOTAL     .          30       .  1.228079E+05  .                  .
...............................................................

MULTIPLE CORRELATION COEFFICIENT =  8.253800E-01

CONSTANT TERM(INTERCEPT) =  3.690478E+04


   COEFFICIENTS     EST OF SD
 -8.6595986E+03   3.5086377E+03
 -3.1853336E+03   2.0939614E+03
 -6.7058524E+03   3.4049073E+03
  6.3034928E+02   1.0446127E+03
 -1.0228344E+04   3.7574227E+03
  3.2799301E+03   2.5669906E+03
  4.4362473E+03   4.6816896E+03
 -1.9235075E+03   4.6394966E+03


 F RATIO(  8, 22  DEGREES OF FREEDOM)=  5.877508E+00

UPPER RT HAND PORTION OF MATRICES ONLY

INVERSE ADJ DATA MOMENT MATRIX
ROW(  1)  6.9187E+03 -6.6065E+02 -5.0060E+03  1.0083E+03  4.6869E+02
-8.3859E+02  6.0114E+03 -5.6340E+03
ROW(  2)  2.4643E+03 -1.2062E+03  5.0306E+02  1.0187E+02  6.9088E+02
 6.1970E+01 -1.4519E+03
ROW(  3)  6.5157E+03 -1.7610E+03 -1.3368E+03  1.1855E+03 -4.9030E+03
 5.4034E+03
ROW(  4)  6.1328E+02  9.3397E+02 -6.6186E+02  6.5211E+02 -9.7282E+02
ROW(  5)  7.9347E+03 -4.7959E+03 -3.9622E+03  2.6049E+03
ROW(  6)  3.7034E+03  2.0486E+03 -2.2883E+03
ROW(  7)  1.2318E+04 -1.1230E+04
ROW(  8)  1.2097E+04

EST COEFFICIENT VAR-COVAR MATRIX
ROW(  1)  1.2311E+07 -1.1755E+06 -8.9073E+06  1.7941E+06  8.3395E+05
-1.4921E+06  1.0696E+07 -1.0025E+07
ROW(  2)  4.3847E+06 -2.1461E+06  8.9510E+05  1.8125E+05  1.2293E+06
 1.1026E+05 -2.5833E+06
ROW(  3)  1.1593E+07 -3.1334E+06 -2.3786E+06  2.1094E+06 -8.7239E+06
 9.6143E+06
ROW(  4)  1.0912E+06  1.6618E+06 -1.1777E+06  1.1603E+06 -1.7309E+06
ROW(  5)  1.4118E+07 -8.5334E+06 -7.0501E+06  4.6349E+06
ROW(  6)  6.5894E+06  3.6451E+06 -4.0715E+06
ROW(  7)  2.1918E+07 -1.9981E+07
ROW(  8)  2.1525E+07
```

RUN 3 (Continued)

```
ADJ DATA CORRELATION MATRIX
ROW(  1)  1.0000E+00 -1.6000E-01 -7.4559E-01  4.8950E-01  6.3257E-02
-1.6567E-01  6.5116E-01 -6.1583E-01
ROW(  2)  1.0000E+00 -3.0101E-01  4.0921E-01  2.3037E-02 -2.2870E-01
 1.1248E-02 -2.6591E-01
ROW(  3)  1.0000E+00 -8.8097E-01 -1.8592E-01  2.4134E-01 -5.4727E-01
 6.0861E-01
ROW(  4)  1.0000E+00  4.2339E-01 -4.3918E-01  2.3725E-01 -3.5716E-01
ROW(  5)  1.0000E+00 -8.8472E-01 -4.0077E-01  2.6588E-01
ROW(  6)  1.0000E+00  3.0331E-01 -3.4187E-01
ROW(  7)  1.0000E+00 -9.1990E-01
ROW(  8)  1.0000E+00


READY
?STOP


USED   14.76 UNITS
BYE
0014.89  CRU     0000.37  TCH    0009.14  KC

OFF AT 14:20EST 11/21/74
```

Texas Gulf

Data Set

TGX4

```
TGX4          10:48EST     12/09/74

100  135,806,1118,845,991,821,863,821,846
101  120,805,1115,846,992,822,863,822,846
102  134,806,1118,845,992,821,863,821,846
103  132,800,1118,843,994,822,865,820,847
104  140,803,1113,845,988,816,859,815,842
105  135,803,1117,840,991,818,860,818,842
106  222,797,1104,830,1001,832,886,834,866
107  188,795,1098,828,1001,829,884,832,863
108  200,795,1097,826,1000,826,883,830,862
109  120,806,1125,849,984,811,849,823,850
110  127,803,1117,843,982,808,848,820,849
111  130,805,1120,845,981,808,845,818,848
112  140,808,1128,848,980,800,830,810,838
113  141,811,1134,855,983,808,842,821,847
114  127,809,1130,853,986,813,851,827,851
115  100,799,1121,842,979,816,852,826,849
116
117  125,799,1120,850,950,763,763,769,786
118  132,801,1128,840,968,790,808,795,822
119  120,803,1125,840,969,800,830,801,830
120  110 ,808,1130,841,970,800,830,803,831
121  70,802,1103,842,977,811,846,801,828
122  80,800,1091,839,975,811,845,805,827
123  60,778,1103,828,960,804,834,806,819
124  118,805,1109,846,999,826,869,821,849
125  110,806,1113,849,999,826,868,821,846
126  110,809,1117,850,999,826,867,821,846
127  200,793,1126,791,791,800,812,793,821
128  130,800,1120,848,980,803,815,818,837
129  95,798,1118,847,983,817,848,833,850
130  100,803,1128,834,972,814,850,830,855
```

STANDARD STATISTICS

```
                 DESCRIPTIVE STATISTICS FØR Y1

NUMBER ØF ØBSERVATIØNS ........................................  30

MEAN = XBR = SUM(X(I))/N ..............................      128.37

MEDIAN ................................................      127.00

RANGE .................................................      162.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ............................      1255.2

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S .........      35.428

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.......      1298.4

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ...............      36.034

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ............     0.77832

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..............      3.8945


            2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
            -----------------------------------------------------------
                        MEAN                        STANDARD DEVIATIØN
            ------------------------          ------------------------
CØNFIDENCE    LØWER        UPPER                LØWER          UPPER
  LEVEL       LIMIT        LIMIT                LIMIT          LIMIT

  90.0%        117.19       139.55               29.746         46.113
  95.0%        114.91       141.82               28.698         48.441
  99.0%        110.23       146.50               26.823         53.570
                                          FØR A NØRMAL DISTRIBUTIØN
```

```
             Y1
             INPUT           ØRDERED          CUMULATIVE      CUMULATIVE
              DATA            DATA            PERCENTAGE        NØRMAL        DIFFERENCE

      1       135               60               3.226            2.890          -0.336
      2       120               70               6.452            5.264          -1.188
      3       134               80               9.677            8.976          -0.702
      4       132               95              12.903           17.723           4.820
      5       140              100              19.355           21.558           2.203
      6       135              100              19.355           21.558           2.203
      7       222              110              29.032           30.513           1.481
      8       188              110              29.032           30.513           1.481
      9       200              110              29.032           30.513           1.481
     10       120              118              32.258           38.679           6.421
     11       127              120              41.935           40.820          -1.116
     12       130              120              41.935           40.820          -1.116
     13       140              120              41.935           40.820          -1.116
     14       141              125              45.161           46.278           1.117
     15       127              127              51.613           48.487          -3.126
     16       100              127              51.613           48.487          -3.126
     17       125              130              58.065           51.808          -6.257
     18       132              130              58.065           51.808          -6.257
     19       120              132              64.516           54.016         -10.500
     20       110              132              64.516           54.016         -10.500
     21        70              134              67.742           56.212         -11.530
     22        80              135              74.194           57.303         -16.891
     23        60              135              74.194           57.303         -16.891
     24       118              140              80.645           62.659         -17.986
     25       110              140              80.645           62.659         -17.986
     26       110              141              83.871           63.705         -20.166
     27       200              188              87.097           95.103           8.006
     28       130              200              93.548           97.659           4.111
     29        95              200              93.548           97.659           4.111
     30       100              222              96.774           99.532           2.758

             0.2296 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                 DESCRIPTIVE STATISTICS FOR X1

NUMBER OF OBSERVATIONS ....................................... 30

MEAN = XBR = SUM(X(I))/N ........................          801.87

MEDIAN ..........................................          803.00

RANGE ...........................................          33.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR .......................          39.116

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ......        6.2542

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.....       40.464

ADJUSTED STANDARD DEVIATION = SQRT(AVR) ..........          6.3612

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ........        -1.7507

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ..........         7.6792

              2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
              ----------------------------------------------------------
                         MEAN                     STANDARD DEVIATION
              -------------------------    -------------------------
CONFIDENCE       LOWER         UPPER         LOWER         UPPER
  LEVEL          LIMIT         LIMIT         LIMIT         LIMIT

  90.0%          799.89        803.84        5.2511        8.1404
  95.0%          799.49        804.24        5.0661        8.5514
  99.0%          798.67        805.07        4.7352        9.4569
                                           FOR A NORMAL DISTRIBUTION
```

```
            X1
           INPUT          ØRDERED         CUMULATIVE     CUMULATIVE
            DATA           DATA           PERCENTAGE       NØRMAL       DIFFERENCE

    1       806            778              3.226           0.009          -3.217
    2       805            793              6.452           8.168           1.716
    3       806            795             12.903          14.019           1.116
    4       800            795             12.903          14.019           1.116
    5       803            797             16.129          22.212           6.083
    6       803            798             19.355          27.164           7.809
    7       797            799             25.806          32.612           6.806
    8       795            799             25.806          32.612           6.806
    9       795            800             35.484          38.459           2.975
   10       806            800             35.484          38.459           2.975
   11       803            800             35.484          38.459           2.975
   12       805            801             38.710          44.581           5.872
   13       808            802             41.935          50.836           8.901
   14       811            803             58.065          57.070          -0.994
   15       809            803             58.065          57.070          -0.994
   16       799            803             58.065          57.070          -0.994
   17       799            803             58.065          57.070          -0.994
   18       801            803             58.065          57.070          -0.994
   19       803            805             67.742          68.884           1.142
   20       808            805             67.742          68.884           1.142
   21       802            805             67.742          68.884           1.142
   22       800            806             80.645          74.208          -6.437
   23       778            806             80.645          74.208          -6.437
   24       805            806             80.645          74.208          -6.437
   25       806            806             80.645          74.208          -6.437
   26       809            808             87.097          83.252          -3.844
   27       793            808             87.097          83.252          -3.844
   28       800            809             93.548          86.894          -6.655
   29       798            809             93.548          86.894          -6.655
   30       803            811             96.774          92.447          -4.327

          0.1374 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FOR X2

NUMBER OF OBSERVATIONS ..........................................  30

MEAN = XBR = SUM(X(I))/N ................................      1116.8

MEDIAN ..................................................      1118.0

RANGE ...................................................      43.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................      111.43

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........      10.556

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........      115.27

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................      10.736

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............    -0.66769

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................      2.7854


               2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
               ----------------------------------------------------------
                         MEAN                       STANDARD DEVIATION
               ------------------------        -----------------------
CONFIDENCE        LOWER        UPPER              LOWER         UPPER
  LEVEL           LIMIT        LIMIT              LIMIT         LIMIT

  90.0%          1113.5       1120.1             8.8628        13.739
  95.0%          1112.8       1120.8             8.5505        14.433
  99.0%          1111.4       1122.2             7.9920        15.961
                                       FOR A NORMAL DISTRIBUTION
```

```
            X2
            INPUT        ØRDERED         CUMULATIVE     CUMULATIVE
             DATA        DATA            PERCENTAGE       NØRMAL      DIFFERENCE

   1        1118          1091             3.226           0.813        -2.413
   2        1115          1097             6.452           3.258        -3.194
   3        1118          1098             9.677           3.997        -5.681
   4        1118          1103            16.129           9.933        -6.196
   5        1113          1103            16.129           9.933        -6.196
   6        1117          1104            19.355          11.659        -7.696
   7        1104          1109            22.581          23.376         0.796
   8        1098          1113            29.032          36.169         7.137
   9        1097          1113            29.032          36.169         7.137
  10        1125          1115            32.258          43.343        11.085
  11        1117          1117            41.935          50.743         8.808
  12        1120          1117            41.935          50.743         8.808
  13        1128          1117            41.935          50.743         8.808
  14        1134          1118            54.839          54.450        -0.389
  15        1130          1118            54.839          54.450        -0.389
  16        1121          1118            54.839          54.450        -0.389
  17        1120          1118            54.839          54.450        -0.389
  18        1128          1120            64.516          61.717        -2.799
  19        1125          1120            64.516          61.717        -2.799
  20        1130          1120            64.516          61.717        -2.799
  21        1103          1121            67.742          65.217        -2.525
  22        1091          1125            74.194          77.750         3.556
  23        1103          1125            74.194          77.750         3.556
  24        1109          1126            77.419          80.425         3.006
  25        1113          1128            87.097          85.157        -1.940
  26        1117          1128            87.097          85.157        -1.940
  27        1126          1128            87.097          85.157        -1.940
  28        1120          1130            93.548          89.055        -4.493
  29        1118          1130            93.548          89.055        -4.493
  30        1128          1134            96.774          94.543        -2.232

             0.1741 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FØR X3

NUMBER ØF ØBSERVATIØNS ...........................................  30

MEAN = XBR = SUM(X(I))/N ................................     840.93

MEDIAN ..................................................     844.00

RANGE ...................................................     64.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................     137.60

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........     11.730

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........     142.34

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................     11.931

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............    -2.5867

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     11.321

              2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
              ---------------------------------------------------------
                         MEAN                        STANDARD DEVIATIØN
              -----------------------------     ---------------------------
CØNFIDENCE       LØWER         UPPER               LØWER           UPPER
 LEVEL           LIMIT         LIMIT               LIMIT           LIMIT

  90.0%         837.23        844.63              9.8487          15.268
  95.0%         836.48        845.39              9.5016          16.039
  99.0%         834.93        846.94              8.8810          17.737
                                            FØR A NØRMAL DISTRIBUTIØN
              X3
              INPUT           ØRDERED        CUMULATIVE     CUMULATIVE
               DATA            DATA          PERCENTAGE       NØRMAL      DIFFERENCE

      1       845              791              3.226          0.001        -3.224
      2       846              826              6.452         10.534         4.083
      3       845              828             12.903         13.917         1.014
      4       843              828             12.903         13.917         1.014
      5       845              830             16.129         17.973         1.844
      6       840              834             19.355         28.057         8.703
      7       830              839             22.581         43.563        20.983
      8       828              840             32.258         46.882        14.624
      9       826              840             32.258         46.882        14.624
     10       849              840             32.258         46.882        14.624
     11       843              841             35.484         50.223        14.739
     12       845              842             41.935         53.562        11.627
     13       848              842             41.935         53.562        11.627
     14       855              843             48.387         56.876         8.489
     15       853              843             48.387         56.876         8.489
     16       842              845             61.290         63.340         2.049
     17       850              845             61.290         63.340         2.049
     18       840              845             61.290         63.340         2.049
     19       840              845             61.290         63.340         2.049
     20       841              846             67.742         66.446        -1.296
     21       842              846             67.742         66.446        -1.296
     22       839              847             70.968         69.445        -1.523
     23       828              848             77.419         72.318        -5.101
     24       846              848             77.419         72.318        -5.101
     25       849              849             83.871         75.052        -8.819
     26       850              849             83.871         75.052        -8.819
     27       791              850             90.323         77.636       -12.687
     28       848              850             90.323         77.636       -12.687
     29       847              853             93.548         84.409        -9.140
     30       834              855             96.774         88.081        -8.693

               0.2356 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FOR X4

NUMBER OF OBSERVATIONS ........................................  30

MEAN = XBR = SUM(X(I))/N ................................     977.23

MEDIAN ..................................................     983.00

RANGE ...................................................     210.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................     1349.5

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........     36.736

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........     1396.0

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................     37.364

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............    -4.3015

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................     22.063

              2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
              ---------------------------------------------------------
                          MEAN                      STANDARD DEVIATION
              -------------------------      -------------------------
CONFIDENCE     LOWER         UPPER             LOWER          UPPER
  LEVEL        LIMIT         LIMIT             LIMIT          LIMIT

  90.0%         965.64        988.82            30.844         47.815
  95.0%         963.28        991.19            29.757         50.229
  99.0%         958.43        996.04            27.813         55.547
                                              FOR A NORMAL DISTRIBUTION
```

```
             X4
             INPUT          ØRDERED        CUMULATIVE     CUMULATIVE
              DATA           DATA          PERCENTAGE       NØRMAL       DIFFERENCE

     1        991             791             3.226          0.000          -3.226
     2        992             950             6.452         23.304          16.852
     3        992             960             9.677         32.232          22.554
     4        994             968            12.903         40.241          27.338
     5        988             969            16.129         41.280          25.151
     6        991             970            19.355         42.325          22.970
     7       1001             972            22.581         44.430          21.850
     8       1001             975            25.806         47.617          21.810
     9       1000             977            29.032         49.751          20.719
    10        984             979            32.258         51.886          19.628
    11        982             980            38.710         52.951          14.242
    12        981             980            38.710         52.951          14.242
    13        980             981            41.935         54.015          12.079
    14        983             982            45.161         55.076           9.914
    15        986             983            51.613         56.133           4.520
    16        979             983            51.613         56.133           4.520
    17        950             984            54.839         57.186           2.347
    18        968             986            58.065         59.275           1.211
    19        969             988            61.290         61.339           0.048
    20        970             991            67.742         64.373          -3.369
    21        977             991            67.742         64.373          -3.369
    22        975             992            74.194         65.366          -8.828
    23        960             992            74.194         65.366          -8.828
    24        999             994            77.419         67.319         -10.100
    25        999             999            87.097         71.991         -15.106
    26        999             999            87.097         71.991         -15.106
    27        791             999            87.097         71.991         -15.106
    28        980            1000            90.323         72.885         -17.438
    29        983            1001            96.774         73.764         -23.010
    30        972            1001            96.774         73.764         -23.010

             0.3024 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FOR X5

NUMBER OF OBSERVATIONS .........................................  30

MEAN = XBR = SUM(X(I))/N ................................      812.07

MEDIAN ..................................................      813.50

RANGE ...................................................      69.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................      186.33

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ...........      13.650

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........      192.75

ADJUSTED STANDARD DEVIATION = SQRT(AVR) .................$     13.884

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............     -1.4408

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................      6.2938

              2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
                         MEAN                       STANDARD DEVIATION
              -------------------------          -------------------------
CONFIDENCE        LOWER        UPPER              LOWER         UPPER
  LEVEL           LIMIT        LIMIT              LIMIT         LIMIT

   90.0%          807.76       816.37             11.461        17.767
   95.0%          806.88       817.25             11.057        18.664
   99.0%          805.08       819.05             10.335        20.640
                                               FOR A NORMAL DISTRIBUTION
```

```
          X5
          INPUT      ORDERED      CUMULATIVE    CUMULATIVE
           DATA       DATA        PERCENTAGE      NORMAL      DIFFERENCE

   1      821          763           3.226         0.020        -3.205
   2      822          790           6.452         5.598        -0.853
   3      821          800          19.355        19.239        -0.116
   4      822          800          19.355        19.239        -0.116
   5      816          800          19.355        19.239        -0.116
   6      818          800          19.355        19.239        -0.116
   7      832          803          22.581        25.686         3.106
   8      829          804          25.806        28.061         2.255
   9      826          808          35.484        38.479         2.996
  10      811          808          35.484        38.479         2.996
  11      808          808          35.484        38.479         2.996
  12      808          811          45.161        46.938         1.777
  13      800          811          45.161        46.938         1.777
  14      808          811          45.161        46.938         1.777
  1=      813          813          48.387        52.680         4.293
  16      816          814          51.613        55.537         3.925
  17      763          816          58.065        61.153         3.088
  18      790          816          58.065        61.153         3.088
  19      800          817          61.290        63.883         2.593
  20      800          818          64.516        66.544         2.028
  21      811          821          70.968        74.003         3.036
  22      811          821          70.968        74.003         3.036
  23      804          822          77.419        76.284        -1.135
  24      826          822          77.419        76.284        -1.135
  25      826          826          90.323        84.221        -6.102
  26      826          826          90.323        84.221        -6.102
  27      800          826          90.323        84.221        -6.102
  28      803          826          90.323        84.221        -6.102
  29      817          829          93.548        88.870        -4.678
  30      814          832          96.774        92.446        -4.328

          0.1257 = KOLMOGOROV-SMIRNOV STATISTIC
```

```
               DESCRIPTIVE STATISTICS FØR X6

NUMBER ØF ØBSERVATIØNS ............................................   30

MEAN = XBR = SUM(X(I))/N ...................................     847.60

MEDIAN .....................................................     849.50

RANGE ......................................................     123.00

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR .................................     628.57

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ..............     25.071

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR............     650.25

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) ....................     25.500

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) .................    -1.2096

KURTØSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ...................     5.3209

             2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
             ---------------------------------------------------------
                         MEAN                      STANDARD DEVIATIØN
             -------------------------       -------------------------
CØNFIDENCE     LØWER          UPPER            LØWER          UPPER
  LEVEL        LIMIT          LIMIT            LIMIT          LIMIT

  90.0%         839.69         855.51           21.050         32.632
  95.0%         838.08         857.12           20.308         34.280
  99.0%         834.77         860.43           18.982         37.910
                                             FØR A NØRMAL DISTRIBUTIØN
```

```
            X6
            INPUT           ØRDERED         CUMULATIVE      CUMULATIVE
             DATA            DATA           PERCENTAGE        NØRMAL        DIFFERENCE

    1       863              763              3.226            0.045          -3.180
    2       863              808              6.452            6.022          -0.430
    3       863              812              9.677            8.135          -1.543
    4       865              815             12.903           10.055          -2.848
    5       859              830             22.581           24.504           1.923
    6       860              830             22.581           24.504           1.923
    7       886              830             22.581           24.504           1.923
    8       884              834             25.806           29.690           3.884
    9       883              842             29.032           41.309          12.277
   10       849              845             35.484           45.939          10.456
   11       848              845             35.484           45.939          10.456
   12       845              846             38.710           47.498           8.789
   13       830              848             45.161           50.626           5.464
   14       842              848             45.161           50.626           5.464
   15       851              849             48.387           52.189           3.802
   16       852              850             51.613           53.749           2.136
   17       763              851             54.839           55.304           0.465
   18       808              852             58.065           56.850          -1.215
   19       830              859             61.290           67.258           5.968
   20       830              860             64.516           68.661           4.145
   21       846              863             74.194           72.705          -1.488
   22       845              863             74.194           72.705          -1.488
   23       834              863             74.194           72.705          -1.488
   24       869              865             77.419           75.249          -2.170
   25       868              867             80.645           77.661          -2.984
   26       867              868             83.871           78.814          -5.056
   27       812              869             87.097           79.933          -7.164
   28       815              883             90.323           91.747           1.424
   29       848              884             93.548           92.328          -1.221
   30       850              886             96.774           93.395          -3.379

              0.1594 = KØLMØGØRØV-SMIRNØV STATISTIC
```

```
                DESCRIPTIVE STATISTICS FØR X7

NUMBER OF ØBSERVATIØNS ........................................  30

MEAN = XBR = SUM(X(I))/N ................................    815.83

MEDIAN ..................................................    820.50

RANGE ...................................................    65.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR ..............................    193.87

UNADJUSTED STANDARD DEVIATIØN = SQRT(UVR) = S ...........    13.924

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR.........    200.56

ADJUSTED STANDARD DEVIATIØN = SQRT(AVR) .................    14.162

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ..............   -1.3548

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) ................    5.1429

             2-SIDED CØNFIDENCE INTERVALS ØN MEAN & STANDARD DEVIATIØN
             ------------------------------------------------------------
                        MEAN                       STANDARD DEVIATIØN
             -------------------------        ---------------------------
CØNFIDENCE      LØWER        UPPER              LØWER         UPPER
  LEVEL         LIMIT        LIMIT              LIMIT         LIMIT

  90.0%         811.44       820.23             11.690        18.123
  95.0%         810.55       821.12             11.279        19.038
  99.0%         808.71       822.96             10.542        21.054
                                             FØR A NØRMAL DISTRIBUTIØN
```

```
          X7
          INPUT          ORDERED       CUMULATIVE     CUMULATIVE
           DATA           DATA         PERCENTAGE       NORMAL      DIFFERENCE

  1        821            769            3.226          0.047        -3.179
  2        822            793            6.452          5.345        -1.107
  3        821            795            9.677          7.063        -2.614
  4        820            801           16.129         14.745        -1.384
  5        815            801           16.129         14.745        -1.384
  6        818            803           19.355         18.242        -1.113
  7        834            805           22.581         22.215        -0.366
  8        832            806           25.806         24.373        -1.433
  9        830            810           29.032         34.020         4.988
 10        823            815           32.258         47.654        15.396
 11        820            818           41.935         56.080        14.144
 12        818            818           41.935         56.080        14.144
 13        810            818           41.935         56.080        14.144
 14        821            820           48.387         61.570        13.183
 15        827            820           48.387         61.570        13.183
 16        826            821           67.742         64.238        -3.504
 17        769            821           67.742         64.238        -3.504
 18        795            821           67.742         64.238        -3.504
 19        801            821           67.742         64.238        -3.504
 20        803            821           67.742         64.238        -3.504
 21        801            821           67.742         64.238        -3.504
 22        805            822           70.968         66.838        -4.130
 23        806            823           74.194         69.359        -4.834
 24        821            826           77.419         76.359        -1.061
 25        821            827           80.645         78.480        -2.165
 26        821            830           87.097         84.143        -2.954
 27        793            830           87.097         84.143        -2.954
 28        818            832           90.323         87.318        -3.004
 29        833            833           93.548         88.728        -4.821
 30        830            834           96.774         90.022        -6.752

        0.2275 = KOLMOGOROV-SMIRNOV STATISTIC
```

```
                    DESCRIPTIVE STATISTICS FOR X8

NUMBER OF OBSERVATIONS ........................................   30

MEAN = XBR = SUM(X(I))/N ...............................       841.30

MEDIAN .................................................       846.00

RANGE ..................................................       80.000

UNADJUSTED (BIASED) VARIANCE =
 SUM((X(I)-XBR)**2)N = UVR .............................       244.21

UNADJUSTED STANDARD DEVIATION = SQRT(UVR) = S ............     15.627

ADJUSTED (UNBIASED) VARIANCE = UVR*N/(N-1) = AVR..........     252.63

ADJUSTED STANDARD DEVIATION = SQRT(AVR) ..................     15.894

SKEWNESS = SUM((X(I)-XBR)**3)/(N*UVR**1.5) ...............    -1.4164

KURTOSIS = SUM((X(I)-XBR)**4)/(N*UVR**2) .................     6.0694


            2-SIDED CONFIDENCE INTERVALS ON MEAN & STANDARD DEVIATION
            ---------------------------------------------------------
                         MEAN                      STANDARD DEVIATION
            ------------------------       ------------------------
CONFIDFNCE     LOWER        UPPER             LOWER          UPPER
 LEVEL         LIMIT        LIMIT             LIMIT          LIMIT

  90.0%         836.37       846.23             13.121         20.340
  95.0%         835.36       847.24             12.658         21.367
  99.0%         833.30       849.30             11.832         23.630
                                           FOR A NORMAL DISTRIBUTION
```

```
          X8
          INPUT          ØRDERED       CUMULATIVE    CUMULATIVE
           DATA           DATA         PERCENTAGE      NØRMAL      DIFFERENCE

   1      846             786             3.226         0.025       -3.201
   2      846             819             6.452         8.031        1.579
   3      846             821             9.677        10.077        0.399
   4      847             822            12.903        11.232       -1.671
   5      842             827            16.129        18.414        2.285
   6      842             828            19.355        20.136        0.781
   7      866             830            22.581        23.856        1.275
   8      863             831            25.806        25.848        0.042
   9      862             837            29.032        39.337       10.305
  10      850             838            32.258        41.776        9.518
  11      849             842            38.710        51.756       13.047
  12      848             842            38.710        51.756       13.047
  13      838             846            54.839        61.627        6.788
  14      847             846            54.839        61.627        6.788
  15      851             846            54.839        61.627        6.788
  16      849             846            54.839        61.627        6.788
  17      786             846            54.839        61.627        6.788
  18      822             847            61.290        64.006        2.716
  19      830             847            61.290        64.006        2.716
  20      831             848            64.516        66.332        1.816
  21      828             849            74.194        68.597       -5.597
  22      827             849            74.194        68.597       -5.597
  23      819             849            74.194        68.597       -5.597
  24      849             850            80.645        70.794       -9.852
  25      846             850            80.645        70.794       -9.852
  26      846             851            83.871        72.916      -10.955
  27      821             855            87.097        80.564       -6.533
  28      837             862            90.323        90.360        0.038
  29      850             863            93.548        91.391       -2.157
  30      855             866            96.774        93.991       -2.783

          0.2163 = KØLMØGØRØV-SMIRNØV STATISTIC
```

STATISTICAL ANALYSIS
OF
DUAL CONVERSION ACID PLANTS

Catalytic Project 42460

EPA Contract 68-02-1322

by

Dr. D. E. Nixon

1.1 Introduction

This report is concerned with analyses of and comments on several data sets containing information on sulfur dioxide emission at sulfuric acid producing plants.

Data sets, figures and other computer results contained in the report and are divided into three sections: A, B, and C. Each section represents a different type of analysis using the five data sets provided. The data sets examined were as follows:

Data Set 1: Data from ASARCO sulfuric acid plant. (A-1,2)
Data Set 2: Data from ASARCO sulfuric acid plant. (A-3)
Data Set 3: Data from Texas Gulf H_2SO_4 No. 1 plant.
Data Set 4: Data from Texas Gulf H_2SO_4 No. 2 plant.
Data Set 5: Data relating to a start-up analysis described in Figure VI-1, page VI-6 Appendix VI: "Analysis of Dual-Absorption Acid Plant Continuous SO_2 Monitoring Data."

These data sets are referenced in this section according to the above numbers (1)-(5).

By way of further introduction it should be reported that the writer of this section has been completely unbiased in presentations herein from the point of view of his lack of knowledge of the operations of sulfuric acid plants. Thus, some of these results may be refuted from theoretical considerations. Some additional insights

DATA SET 1 AND 2

COMPUTER RUN A-1

```
  1   825     0   850   955   770   755   715   715  2130  7.21
  2   830     0   845   880   780   815   775   785    23  1.95
  3   830     0   835   850   760   770   760   760    55  3.81
  4   825     0   850   895   765   765   750   760   894  5.61
  5   830     0   840   870   790   795   775   765   435  5.28
  6   825     0   850   905   780   815   785   795   132  4.77
  7   820     0   850   870   800   825   785   790   175  4.18
  8   825     0   850   880   785   785   780   790    33  2.29
  9   820     0   820   840   740   740   738   742    26  3.10
 10   816  1016   826   880   754   750   752   754    93  0.00
 11   825  1100   850   975   835   860   825   795   191  0.00
 12   820   980   820   865   775   795   760   760   110  0.00
 13   650   665   675   700   690   700   705   745    11  0.00
 14   840  1055   790   750   615   625   700   820  1012  0.00
 15   815  1090   800   925   770   770   705   690   125  0.00
 16   810  1055   825   905   790   805   775   765    28  0.00
 17   816  1094   812   912   764   804   764   796    48  0.00
 18   824  1004   818   876   768   762   742   742    31  0.00
 19   824  1114   834   922   768   774   758   764   182  0.00
 20   824  1078   836   914   792   782   760   760    28  0.00
 21   822  1026   834   886   762   770   758   762    38  0.00
 22   820  1078   832   900   768   794   754   762    24  0.00
 23   824  1136   840   962   800   822   782   782   102  0.00
 24   820  1070   820   850   730   710   690   700   131  4.58
 25   820  1030   820   880   770   770   735   730   139  4.95
 26   825  1080   840   920   800   815   795   800   124  4.74
 27   820  1040   840   910   800   815   745   800    48  3.03
 28   825  1000   820   860   790   780   750   765    51  4.38
 29   825   955   820   845   730   725   705   710   701  5.34
 30   830  1000   830   860   795   780   740   730    94  4.34
 31   830  1015   830   870   770   770   750   755    30  5.64
 32   830  1070   845   930   805   840   785   775   138  5.08
 33   834   836   734   730   730   800   692   688    16  0.10
 34   844   922   754   744   700   800   700   698   209  3.81
 35   828  1042   824   864   710   758   662   686    57  3.50
 36   828  1044   818   834   734   778   706   702    80  3.58
 37   815  1060   825   845   735   735   695   685   260  4.70
 38   820  1100   830   870   765   765   735   735    48  4.77
 39   820  1080   840   835   745   745   730   740    61  2.47
 40   825     0   850   840   860   855   790   760   127  2.30
 41   825     0   840   870   830   835   800   820   416  2.94
 42   825     0   855   920   865   865   825   825   657  6.65
 43   840     0   820   805   755   740   670   675     2  0.32
 44   820     0   840   880   755   735   705   705   123  4.15
 45   820     0   845   910   780   770   740   740   137  6.64
 46   820     0   830   870   780   770   760   760    19  3.32
 47   830     0   830   835   695   700   690   720   111  1.91
 48   830     0   840   840   695   710   700   735   268  6.56
 49   820     0   840   910   800   800   770   765    29  4.31
 50   850     0   840   880   770   780   770   780   258  7.22
 51   815     0   830   880   770   790   755   760    28  2.27
 52   780     0   840   745   745   760   725   735  1197  7.24
```

DATA SET 1 AND 2

COMPUTER RUN A-2

53	790	0	800	960	810	750	730	715	213	6.22
54	790	0	800	845	750	785	770	770	18	1.83
55	800	0	800	890	765	785	775	770	26	2.28
56	830	0	830	845	765	785	750	750	136	3.95
57	820	0	840	855	745	760	750	750	24	2.33
58	810	0	835	845	755	750	720	725	1274	6.43
59	815	0	850	920	810	775	745	735	85	3.71
60	820	0	840	870	775	800	770	780	320	1.92
61	820	0	840	850	770	800	750	770	947	3.36
62	810	0	845	905	765	750	710	705	904	5.51
63	835	0	830	875	780	785	765	765	191	3.12
64	820	0	845	865	750	780	750	745	41	0.60
65	815	0	845	865	740	750	715	720	43	1.41
66	810	0	850	890	750	750	715	715	516	4.24
67	825	0	855	895	760	750	735	720	60	1.16
68	778	796	687	766	286	225	825	760	7	0.04
69	818	818	702	694	670	660	606	596	129	3.02
70	0	0	0	0	0	0	0	0	2682	5.69
71	804	914	822	852	736	722	684	678	164	2.58
72	835	1110	830	865	750	735	720	725	43	2.43
73	835	1000	810	840	735	735	720	720	60	3.84
74	835	1015	830	860	780	785	765	755	43	2.23
75	835	1010	830	870	790	780	760	765	2463	7.89
76	825	1070	830	955	825	790	770	755	222	5.02
77	825	1015	765	820	670	790	680	735	3	0.08
78	806	850	804	784	754	730	666	640	432	0.91
79	816	824	770	772	704	710	674	664	2145	4.86
80	744	840	764	760	710	700	652	642	873	0.07
81	666	822	720	754	684	692	638	640	1863	0.08
82	835	955	785	755	665	725	670	660	255	1.40
83	825	1080	820	885	720	690	675	685	1695	5.65
84	825	1030	830	875	765	775	745	740	85	3.27
85	820	995	830	860	750	750	740	740	212	3.62
86	740	660	670	780	710	755	690	715	16	0.50
87	790	760	670	690	680	710	680	690	0	0.33
88	830	1075	825	870	745	740	700	695	1311	4.81
89	815	950	835	855	745	735	710	705	21	2.71
90	826	920	816	888	778	770	734	730	54	1.98
91	830	1030	845	920	790	765	735	725	1177	5.91
92	810	945	830	930	785	780	755	745	18	2.61
93	550	760	630	760	665	725	625	705	49	0.05
94	710	690	615	635	630	665	630	635	21	0.06
95	810	1030	780	755	635	640	640	645	3107	4.98
96	805	980	800	820	700	690	650	640	3092	4.09
97	835	1065	840	890	765	755	710	710	995	5.06
98	825	1010	845	915	805	800	775	765	213	5.41
99	825	1050	850	920	810	800	785	775	89	3.56
100	830	990	820	860	750	750	750	760	32	2.88
101	860	1090	830	845	725	715	690	685	1088	3.04
102	835	1090	845	910	775	760	720	710	970	5.87
103	845	1075	845	890	780	785	755	750	228	5.94
104	840	1080	855	920	810	815	780	779	25	0.09
105	760	750	690	705	805	705	685	690	21	0.09
106	810	955	840	860	770	730	685	680	1009	3.50
107	815	955	845	860	760	725	680	675	350	2.50
108	850	1040	865	915	790	765	735	730	73	4.91

have been gained toward the end of the project period and these are summarized under recommendations Subsection 1.6.

1.2 Data Set (1)

This data (A-1,2) was extracted from a rather large data set from the ASARCO Plant and essentially represents data points associated with upset conditions, during start-up, shutdown and points before and after these occurrences.

Altogether, there were 108 observations on the following variables:

X_1 = First Converter Bed Inlet Temperature in $^{\circ}F$. This is also referenced as BMI1 on some of the computer print-outs in the appendix.

X_2 = First Converter Bed Outlet Temperature in $^{\circ}F$. This is referenced as BMO1.

X_3 = Second Converter Bed Inlet Temperature in $^{\circ}F$. This is referenced as BMI2.

X_4 = Second Converter Bed Outlet Temperature in $^{\circ}F$. This is referenced as BMO_2.

X_5 = Third Converter Bed Inlet Temperature in $^{\circ}F$. This is referenced as BMI3.

X_6 = Third Converter Bed Outlet Temperature in $^{\circ}F$. This is referenced as BMO3.

X_7 = Fourth Converter Bed Inlet Temperature in $^{\circ}F$. This is referenced as BMI4.

X_8 = Fourth Converter Bed Outlet Temperature in $^{\circ}F$. This is referenced as BMO4.

X_9 = Percent SO_2 Entrance to Converter. This is referenced as PSO2E.

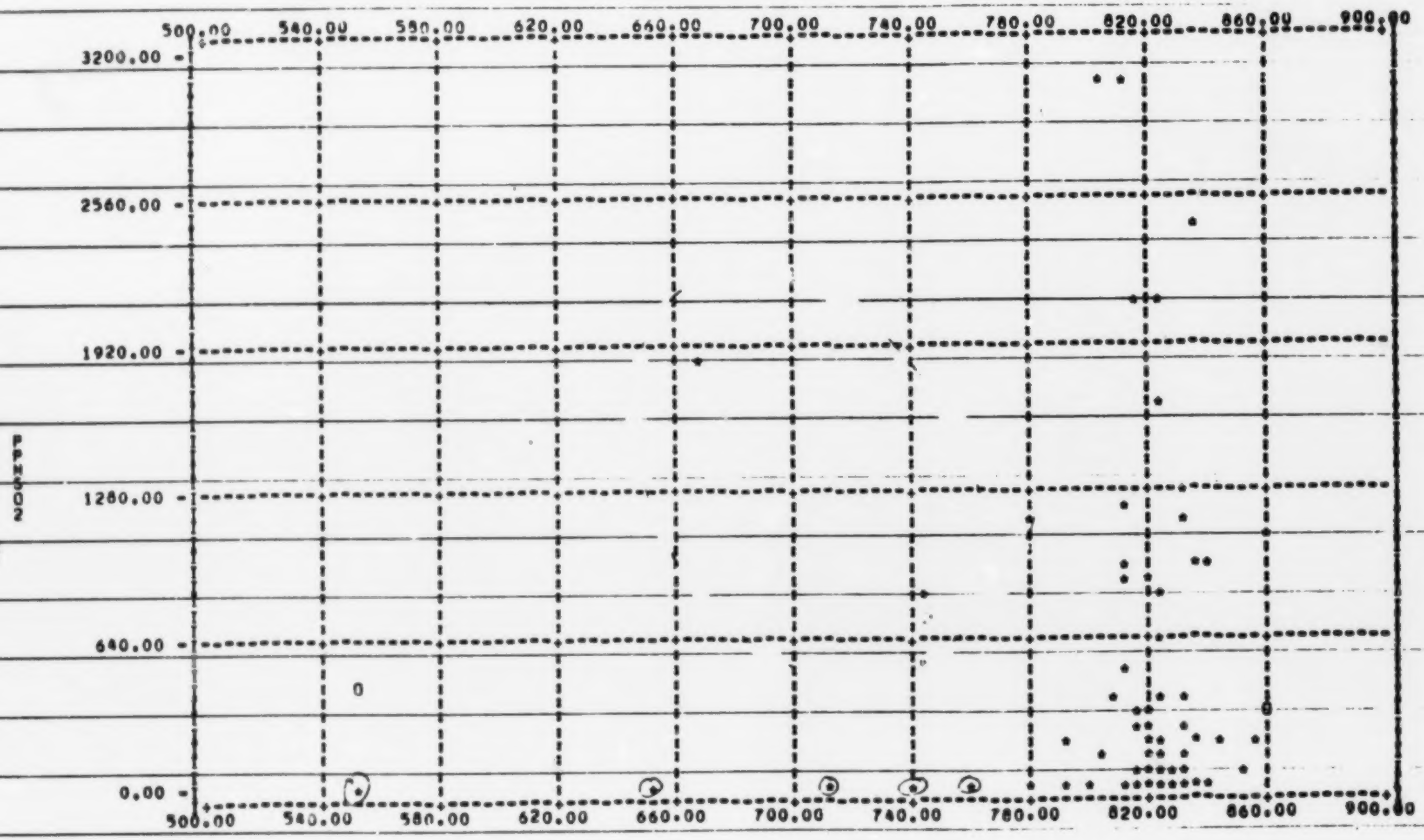
Y = Parts per million SO_2 - exit stack. This is referenced as $PPMSO_2$.

In A-1, 2 these variables are listed for each observation in the above order with the exception that X_9 and Y are interchanged. Data values with a value of 0 denote missing observation (these were not recorded on original charts). Of the 108 points, only 54 contained complete data.

As a first attempt to explain the dependent variable Y in terms of these processes parameters simple correlations were computed. Also scatter plots such as A-4 were obtained. Following are the simple correlations.

Correlation of Y with	Correlation	N
X_1	-0.0214	107
X_2	0.0265	70
X_3	0.0147	107
X_4	-0.1112	107
X_5	-0.1356	107
X_6	-0.1995	107
X_7	-0.3390	107
X_8	-0.3390	107
X_9	0.4030	94

```
  JOB DEF= ******                                                                                PAGE    7
 PROC DEF=  NIXON                                                                               BASIS  4.0
 DATA DEF=   DAVE                                                                                117 5/74
ANALYSIS= REGRES
 DATA SET=      1      READ N=    108,     PROC N =    108,     REJ. N =      0,     SUM WT =    108
```



BWI1

SCATTER PLOT   O=REGRESSION LINE ENDPOINTS

ASARCO

COMPUTER RUN A-4

A-4

```
  JOB DEF= ******
 PROC DEF=  NIXON                                                                                       PAGE    1
 DATA DEF=   DAVE
 ANALYSIS=  MULTR                                                                                      BASIS  4.0
 DATA SET=      1         READ N=    108,      PROC N =    108,      REJ. N =      0,      SUM WT =    108    1/26/75


                     M U L T I P L E   L I N E A R   R E G R E S S I O N   A N A L Y S I S

 GROUP NO  1
 NO OF INDEPENDENT VARIABLES  9

 EPS=  5.0000E-11 FOR SINGULAR MATRIX TEST

 DEPENDENT VARIABLE =      PPMSO2

 MEANS AND STANDARD DEVIATIONS

    VARIABLE          MEAN  ST.DEVIATION

         RMI1      810.6607       48.7637
         RMO1      972.1071      113.1216
         RMI2      800.0893       59.5050
         RMO2      839.4107       70.5922
         RMI3      737.6964       77.2620
         RMO3      740.3571       81.7523
         RMI4      712.7500       47.0606
         RMO4      713.1786       45.1660
        PSO2E        3.2657        2.0048
       PPMSO2      479.2857      771.1871

 NORMAL MATRIX.

           1            2            3            4            5            6

 ROW  1
  130784.5537  198031.0356  114800.6963   92132.8037   68734.2319   59514.7856
   56589.2500   36142.3931    2835.2586
 ROW  2
       0.0000  703807.3572  323522.4641  346223.5359  219401.8213  199957.8572
  135576.5000  131454.9287    8201.3557
 ROW  3
       0.0000       0.0000  194746.5535  200774.9465  152486.5178  122978.2144
   80911.2500   67774.1072    4234.7814
 ROW  4
       0.0000       0.0000       0.0000  274079.5537  173751.9819  141322.7856
  124385.7500  120771.8931    4637.7286
 ROW  5
       0.0000       0.0000       0.0000       0.0000  328317.8391  313303.0713
   46236.7500   63587.0359    3483.6571
 ROW  6
       0.0000       0.0000       0.0000       0.0000       0.0000  367588.8572
   26178.0000   62466.4287    2626.0457
 ROW  7
       0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
  121808.5000  106148.5002    1651.7000
 ROW  8
```

COMPUTER RUN A-5

```
      0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
      0.0000 112198.2144   1367.9429
 ROW  9
      0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
      0.0000      0.0000    221.0614

 CORRELATION MATRIX-

           1           2           3           4           5           6

 ROW  1
      1.0000      0.6527      0.7193      0.4866      0.3317      0.2714
      0.4483      0.2984      0.5273     -0.0254
 ROW  2
      0.6527      1.0000      0.8739      0.7883      0.4564      0.3931
      0.4630      0.4678      0.6575      0.0688
 ROW  3
      0.7193      0.8739      1.0000      0.8690      0.6030      0.4596
      0.5253      0.4585      0.6454      0.0473
 ROW  4
      0.4866      0.7883      0.8690      1.0000      0.5792      0.4452
      0.6808      0.6887      0.5958     -0.0749
 ROW  5
      0.3317      0.4564      0.6030      0.5792      1.0000      0.9019
      0.2312      0.3313      0.4089     -0.0966
 ROW  6
      0.2714      0.3931      0.4596      0.4452      0.9019      1.0000
      0.1237      0.3076      0.2913     -0.1624
 ROW  7
      0.4483      0.4630      0.5253      0.6808      0.2312      0.1237
      1.0000      0.9080      0.3183     -0.3345
 ROW  8
      0.2984      0.4678      0.4585      0.6887      0.3313      0.3076
      0.9080      1.0000      0.2747     -0.3950
 ROW  9
      0.5273      0.6575      0.6454      0.5958      0.4089      0.2913
      0.3183      0.2747      1.0000      0.3484
 ROW 10
     -0.0254      0.0688      0.0473     -0.0749     -0.0966     -0.1624
     -0.3345     -0.3950      0.3484      1.0000
```

COMPUTER RUN A-6

```
  JOB DEF= ******                                                                                         PAGE    2
 PROC DEF=  NIXON
 DATA DEF=   DAVE                                                                                        BASIS  4.0
 ANALYSIS=  MULTR                                                                                          1/26/75
 DATA SET=      1         READ N=    108,      PROC N =    108,      REJ. N =      0,      SUM WT =    108


 REGRESSION COEFFICIENTS-

     VARIABLE    COEFFICIENT    BETA COEFFICIENT

     CONSTANT     8289.9130
         BMI1       -4.3215              -0.2733
         BMO1       -0.0110              -0.0016
         BMI2        4.6408               0.3581
         BMO2       -1.6510              -0.1511
         BMI3       -0.7483              -0.0750
         BMO3       -1.5938              -0.1690
         BMI4       -2.6670              -0.1627
         BMO4       -5.1938              -0.3042
        PSO2E      218.3635               0.5677

 STANDARD ERROR OF ESTIMATE.............. =      629.8371
 COEFFICIENT OF DETERMINATION............ =        0.4421
 COEFFICIENT OF DETERMINATION (ADJ)...... =        0.3330
 MULTIPLE CORRELATION COEFFICIENT........ =        0.6649
 MULTIPLE CORRELATION COEFFICIENT (ADJ) = =        0.5770


 STANDARD DEVIATIONS AND T VALUES OF
 REGRESSION COEFFICIENTS-

       VARIABLE    STD DEVIATION        T       STD DEV BETA       F
           BMI1           3.3081    -1.31             0.2092    1.71
           BMO1           1.8609    -0.01             0.2730    0.00
           BMI2           5.5184     0.84             0.4259    0.71
           BMO2           3.8527    -0.43             0.3527    0.18
           BMI3           3.3417    -0.22             0.3348    0.05
           BMO3           3.0583    -0.52             0.3242    0.27
           BMI4           6.6070    -0.40             0.4032    0.16
           BMO4           6.8677    -0.76             0.4022    0.57
          PSO2E          60.4666     3.61             0.1572   13.04

 HIGH ORDER PARTIAL CORRELATION COEFF AND R2-DELETE

     VARIABLE    PARTIAL CORR COEF    R2-DELETE

         BMI1              -0.1891       0.4214
         BMO1              -0.0009       0.4421
         BMI2               0.1231       0.4336
         BMO2              -0.0631       0.4399
         BMI3              -0.0330       0.4415
         BMO3              -0.0766       0.4389
         BMI4              -0.0594       0.4402
         BMO4              -0.1108       0.4352
        PSO2E               0.4700       0.2842
```

COMPUTER RUN A-7

```
ANALYSIS OF VARIANCE TABLE

    SOURCE   D.F.   SUM SQUARES  MEAN SQUARES      F

REGRESSION      9 14462166.4640  1606907.3849   4.05
     ERROR     46 18247956.9648   396694.7166
     TOTAL     55 32710123.4287

CONFIDENCE LEVEL OF F(    9,   46) =  99.93%
```

COMPUTER RUN A-8

```
 JOB DEF= ******                                                                                          PAGE   3
 PROC DEF=  NIXON
 DATA DEF=   DAVE                                                                                         BASIS  4.0
 ANALYSIS=  MULTR                                                                                          1/26/75
 DATA SET=     1        READ N=     108,      PROC N =     108,      REJ. N =      0,      SUM WT =     108



 TABLE OF RESIDUALS

 OBS NO.        ACTUAL       PREDICTED       RESIDUAL

       1      131.0000        983.0255      -852.0255
       2      139.0000        613.3399      -474.3399
       3      124.0000        -45.6514       169.6514
       4       48.0000       -247.1463       295.1463
       5       51.0000        247.9243      -196.9243
       6      701.0000       1021.0425      -320.0425
       7       94.0000        468.7005      -374.7005
       8       30.0000        614.0299      -584.0299
       9      138.0000        126.7155        11.2845
      10       16.0000       -340.6139       356.6139
      11      209.0000        401.0181      -192.0181
      12       57.0000        794.2285      -737.2285
      13       80.0000        583.0778      -503.0778
      14      260.0000       1083.3897      -823.3897
      15       48.0000        621.9257      -573.9257
      16       61.0000        258.3113      -197.3113
      17        7.0000        131.2022      -124.2022
      18      129.0000       1252.5003     -1123.5003
      19      164.0000        729.7839      -565.7839
      20       43.0000        205.2600      -162.2600
      21       60.0000        500.0131      -440.0131
      22       43.0000       -207.0821       250.0821
      23     2463.0000        974.2836      1488.7164
      24      222.0000        232.9389       -10.9389
      25        3.0000       -464.0467       467.0467
      26      432.0000        605.0601      -173.0601
      27     2145.0000       1209.9968       935.0032
      28      873.0000        624.6882       248.3118
      29     1863.0000        876.4568       986.5432
      30      255.0000        505.3111      -250.3111
      31     1695.0000       1294.4426       400.5574
      32       85.0000        196.7098      -111.7098
      33      212.0000        384.2989      -172.2989
      34       16.0000       -272.8890       288.8890
      35        0.0000       -127.9064       127.9064
      36     1311.0000        920.4229       390.5771
      37       21.0000        528.5891      -507.5891
      38       54.0000        -95.0112       149.0112
      39     1177.0000        848.7056       328.2944
      40       18.0000        -48.0342        66.0342
      41       49.0000        602.9972      -553.9972
      42       21.0000        523.3271      -502.3271
      43     3107.0000       1686.9017      1420.0983
      44     3092.0000       1371.1831      1720.8169
      45      995.0000        846.6584       148.3416
      46      213.0000        388.1674      -175.1674
```

COMPUTER RUN A-9

```
  47        89.0000      -83.6445      172.6445
  48        32.0000        2.5969       29.4031
  49      1088.0000      602.0091      485.9909
  50       970.0000      971.3199       -1.3199
  51       228.0000      631.8933     -403.8933
  52        25.0000     -914.6608      939.6608
  53        21.0000      -81.4122      102.4122
  54      1009.0000      923.3783       85.6217
  55       350.0000      761.3673     -411.3673
  56        73.0000      618.9052     -545.9052

DURBIN-WATSON D STATISTIC =     1.3780
```

COMPUTER RUN A-10

Only the correlations between Y and X_7 and X_9 are significant at the five percent level. Since the difference between X_7 and X_8 is insignificant (a fact no doubt characteristic to the upset conditions which the data represent), these two variables are regarded as the same.

It is felt that X_7 is not influencing Y but rather this correlation is significant because of the following reason: When the fourth converter bed is finally brought up to temperature, SO_2 emission is lower, the nature of start-up. It should be observed that almost all of the above correlations are based on the full 108 observations, unfortunately not the case on omitting missing data in fitting the following model:

$$Y = \alpha_0 + \sum_{K=1}^{9} \alpha_K X_K$$

Complete results of this fit are contained in A-5,10. While this regression equation gave a significant fit to the data at the one percent level and the model accounted for approximately 44 percent of the variability in Y, its usefulness in prediction is questionable. The model does seem to predict "rather close" to the high SO_2 emissions, in order of magnitude, but is somewhat more erratic in predicting low to medium SO_2 emissions. The writer would have liked an additional data set having similar characteristics as (1) in order to verify the reproduceability of the model. Since this set was not available, the 108 points were split down the middle and the model refitted to the last 54 points of which 40 were complete. These results are contained in A-11, 15 and they appear to be comparable to the original fit. In each case PSO_2E was the most significant contributing variable to the regression and, in fact it should be noted that the correlation 0.4030 between Y and X_9 compares with the 0.413 reported on page VI-13 of the appendix referenced in the description of Data Set (5). It is understood that the latter correlation was obtained from the larger ASARCO data set with upset conditions removed.

In summary, the high variability in SO_2 emission and its erractic behavior during these upset conditions seems to preclude a satisfactory explanation in terms of the process parameters considered. It is felt that the main reason for the inadequacy of the model in explaining SO_2 emission during upset conditions is due to the fact that data was reported at two-hour intervals and, in fact, since it is possible for a plant to shut down and start up in just a few hours, the few data points recorded does not adequately report the changing nature of SO_2 emission and the process parameters during these times.

1.3 Data Set (3)

This data consisted of 54 observations on the variables described in Section 1.1 except that in this case the

```
 JOB DEF= ******                                                                                          PAGE    1
PROC DEF=  NIXON
DATA DEF=   DAVE                                                                                         BASIS  4.0
ANALYSIS=  MULTR                                                                                           1/26/75
DATA SET=      1        READ N=      54,      PROC N =      54,      REJ. N =       0,      SUM WT =      54



                  M U L T I P L E   L I N E A R   R E G R E S S I O N   A N A L Y S I S

GROUP NO  1
NO OF INDEPENDENT VARIABLES  9

EPS=  5.0000E-11 FOR SINGULAR MATRIX TEST

DEPENDENT VARIABLE =      PPMSO2

MEANS AND STANDARD DEVIATIONS

    VARIABLE         MEAN  ST.DEVIATION

        BMI1     804.3250       56.3780
        BMO1     952.3500      121.8369
        BMI2     792.8750       66.7168
        BMO2     834.0000       76.2849
        BMI3     730.0500       88.0550
        BMO3     726.9500       91.0989
        BMI4     707.4750       50.3215
        BMO4     705.9750       45.9439
       PSO2E       2.9467        2.1432
      PPMSO2     616.3250      872.3052

NORMAL MATRIX-

           1            2            3            4            5            6

ROW  1
 123960.7749  186277.4500  111113.6250   91439.0000   63463.3501   45529.9500
  52450.8250   30778.3250    2587.9223
ROW  2
      0.0000  578925.0999  276390.7500  288911.0000  185349.3000  167903.0999
 108103.3499   96309.3499    6599.8755
ROW  3
      0.0000       0.0000  173594.3750  173043.0000  135667.2500  110911.2500
  67531.3750   50658.8750    3541.1538
ROW  4
      0.0000       0.0000       0.0000  226956.0000  147584.0000  126036.0000
 101927.0000   93282.0000    3734.5700
ROW  5
      0.0000       0.0000       0.0000       0.0000  302393.9001  289166.3000
  24108.8500   38282.0500    2934.3665
ROW  6
      0.0000       0.0000       0.0000       0.0000       0.0000  323661.0999
   4875.8499   37038.8499    2159.8605
ROW  7
      0.0000       0.0000       0.0000       0.0000       0.0000       0.0000
  98757.9749   81956.4749    1149.9119
ROW  8
```

COMPUTER RUN A-11

```
     0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
     0.0000  82322.9749    944.1768
ROW  9
     0.0000      0.0000      0.0000      0.0000      0.0000      0.0000
     0.0000      0.0000    179.1465

CORRELATION MATRIX-

          1           2           3           4           5           6

ROW  1
     1.0000      0.6954      0.7575      0.5452      0.3278      0.2273
     0.4740      0.3047      0.5492      0.0360
ROW  2
     0.6954      1.0000      0.8719      0.7970      0.4430      0.3879
     0.4521      0.4412      0.6481      0.1785
ROW  3
     0.7575      0.8719      1.0000      0.8718      0.5921      0.4679
     0.5158      0.4238      0.6350      0.1136
ROW  4
     0.5452      0.7970      0.8718      1.0000      0.5634      0.4650
     0.6808      0.6824      0.5857     -0.0437
ROW  5
     0.3278      0.4430      0.5921      0.5634      1.0000      0.9243
     0.1395      0.2426      0.3987     -0.0488
ROW  6
     0.2273      0.3879      0.4679      0.4650      0.9243      1.0000
     0.0273      0.2269      0.2836     -0.0872
ROW  7
     0.4740      0.4521      0.5158      0.6808      0.1395      0.0273
     1.0000      0.9089      0.2734     -0.3217
ROW  8
     0.3047      0.4412      0.4238      0.6824      0.2426      0.2269
     0.9089      1.0000      0.2198     -0.3812
ROW  9
     0.5492      0.6481      0.6350      0.5857      0.3987      0.2836
     0.2734      0.2198      1.0000      0.4728
ROW 10
     0.0360      0.1785      0.1136     -0.0437     -0.0488     -0.0872
    -0.3217     -0.3912      0.4728      1.0000
```

COMPUTER RUN A-12

```
JOB DEF= ******                                                                                              PAGE    2
PROC DEF=  NIXON
DATA DEF=   DAVF                                                                                             BASIS  4.0
ANALYSIS=  MULTR                                                                                               1/26/75
DATA SET=       1         READ N=       54.       PROC N =      54.       REJ. N =        0.       SUM WT =      54


REGRESSION COEFFICIENTS-

     VARIABLE   COEFFICIENT   BETA COEFFICIENT

     CONSTANT     9101.5945
         BMI1       -6.6094           -0.4272
         BMO1        1.4117            0.1972
         BMI2        6.7362            0.5152
         BMO2       -5.0010           -0.4374
         BMI3       -2.2924           -0.2314
         BMO3       -0.2240           -0.0234
         BMI4       -1.5612           -0.0901
         BMO4       -5.0505           -0.2664
        PSO2E      281.1312            0.6907

STANDARD ERROR OF ESTIMATE............. =      653.7521
COEFFICIENT OF DETERMINATION........... =        0.5679
COEFFICIENT OF DETERMINATION (ADJ)..... =        0.4383
MULTIPLE CORRELATION COEFFICIENT....... =        0.7536
MULTIPLE CORRELATION COEFFICIENT (ADJ) =        0.6621

STANDARD DEVIATIONS AND T VALUES OF
REGRESSION COEFFICIENTS-

      VARIABLE   STD DEVIATION       T     STD DEV BETA       F
          BMI1          3.7694   -1.75           0.2436    3.08
          BMO1          2.2194    0.64           0.3100    0.40
          BMI2          6.4629    1.04           0.4943    1.09
          BMO2          4.7414   -1.05           0.4146    1.11
          BMI3          4.1790   -0.55           0.4218    0.30
          BMO3          4.3442   -0.05           0.4537    0.00
          BMI4          9.8892   -0.16           0.5705    0.02
          BMO4         10.3395   -0.49           0.5446    0.24
         PSO2E         70.5327    3.99           0.1733   15.89

HIGH ORDER PARTIAL CORRELATION COEFF AND R2-DELETE

     VARIABLE   PARTIAL CORR COEF   R2-DELETE                                        COMPUTER RUN A-13

         BMI1             -0.3050      0.5236
         BMO1              0.1154      0.5621
         BMI2              0.1869      0.5523
         BMO2             -0.1991      0.5519
         BMI3             -0.0997      0.5636
         BMO3             -0.0094      0.5679
         BMI4             -0.0288      0.5676
         BMO4             -0.0890      0.5645
        PSO2E              0.5884      0.3391
```

```
ANALYSIS OF VARIANCE TABLE

    SOURCE   D.F.   SUM SQUARES  MEAN SQUARES       F

REGRESSION     9 16853984.3315  1872664.9257    4.38
     ERROR    30 12821752.4434   427391.7481
     TOTAL    39 29675736.7749

CONFIDENCE LEVEL OF F(    9,   30) =  99.90%
```

-

COMPUTER RUN A-14

```
  JOB DEF= ******                                                                                         PAGE    3
  PROC DEF=  NIXON
  DATA DEF=   DAVE                                                                                        BASIS  4.0
  ANALYSIS=  MULTR                                                                                          1/26/75
  DATA SET=      1        READ N=     54,      PROC N =      54,      REJ. N =       0,      SUM WT =      54


  TABLE OF RESIDUALS

  OBS NO.       ACTUAL      PREDICTED       RESIDUAL

       1        7.0000        52.9019       -45.9019
       2      129.0000      1312.2348     -1183.2349
       3      164.0000       733.0102      -569.0102
       4       43.0000       422.5530      -379.5530
       5       60.0000       713.6462      -653.6462
       6       43.0000       -44.7563        87.7563
       7     2463.0000      1424.7935      1038.2065
       8      222.0000       296.1514       -74.1514
       9        3.0000      -335.9860       338.9860
      10      432.0000       556.0436      -124.0436
      11     2145.0000      1379.9045       765.0955
      12      873.0000       669.8520       203.1480
      13     1863.0000      1005.3818       857.6182
      14      255.0000       765.1248      -510.1248
      15     1695.0000      1535.6025       159.3975
      16       85.0000       403.6012      -318.6012
      17      212.0000       608.4432      -396.4432
      18       16.0000      -595.4884       611.4884
      19        0.0000      -161.5250       161.5250
      20     1311.0000      1209.9191       101.0809
      21       21.0000       619.5270      -598.5270
      22       54.0000      -241.1945       295.1945
      23     1177.0000      1025.1547       151.8453
      24       18.0000      -165.7256       183.7256
      25       49.0000       767.5104      -718.5104
      26       21.0000       578.0504      -557.0504
      27     3107.0000      2219.5275       887.4725
      28     3092.0000      1590.9143      1501.0857
      29      995.0000      1093.3624       -98.3624
      30      213.0000       607.3949      -394.3949
      31       89.0000        74.7855        14.2145
      32       32.0000       143.1099      -111.1099
      33     1088.0000       811.5615       276.4385
      34      970.0000      1250.3745      -280.3745
      35      228.0000      1008.7621      -780.7621
      36       25.0000      -939.6377       964.6377
      37       21.0000      -278.3645       299.3645
      38     1009.0000       999.7026         9.2974
      39      350.0000       776.3480      -426.3480
      40       73.0000       760.3883      -687.3883

  DURBIN-WATSON D STATISTIC =      1.7276
```

COMPUTER RUN A-15

```
  1   806  1125   849   984   811   849   823   850   120  0.67
  2   804  1120   846   984   810   849   823   950   122  0.00
  3   803  1117   843   982   808   845   820   949   127  0.65
  4   803  1117   840   980   805   846   818   946   130  0.00
  5   805  1120   845   981   808   845   818   948   130  0.89
  6   808  1125   846   983   808   848   821   949   130  0.00
  7   808  1128   848   980   800   830   810   838   140  0.91
  8   811  1134   855   983   808   842   821   947   141  0.74
  9   811  1134   855   986   813   850   826   950   139  0.00
 10   809  1130   853   986   813   851   827   851   127  0.71
 11   809   831   854   985   814   850   827   850   131  0.00
 12   799  1121   842   974   816   852   876   849   100  0.75
 13   800  1094   822   889   755   787   772   808    45  0.00
 14   763  1071   830   870   785   779   770   795     0  0.00
 15   807  1122   848   919   741   740   750   769     0  0.00
 16   799     0   850   950   763   762   769   786   125  0.00
 17   801  1129   840   968   796   808   795   812   132  0.73
 18    83  1125     0   969   800   824   801   830   120  0.00
 19   808  1130   841   976   800   830   803   931   110  0.74
 20   803  1125   839   911   802   820   805   937   106  0.00
 21   802  1103   942   977   811   846   801   928    70  0.89
 22   804  1104   942   975   811   846   801   828    90  0.00
 23   860  1091   839   975   811   845   805   927    80  0.83
 24   800  1099   838   971   808   841   802   923     0  0.00
 25   778  1103   828   960   804   834   806   819    60  0.83
 26   803  1133   838   960   809   840   812   826    70  0.00
 27   801  1136   851   969   812   840   815   930    75  0.84
 28   795  1128   842   964   808   836   812   928    55  0.00
 29   795  1105   840   960   804   831   808   824    65  0.93
 30   803  1118   848   980   809   840   806   829    80  0.00
 31   800  1119   841   979   816   850   810   931    80  0.89
 32   800  1118   840   979   812   849   804   930    80  0.00
 33   800  1101   944   985   810   848   800   924    90  0.90
 34   801  1100   842   989   812   850   807   830    90  0.00
 35   801  1101   843   986   810   849   803   828    92  0.87
 36   800  1102   841   987   809   848   804   928    75  0.00
 37   800  1104   842   987   810   848   805   929    95  0.86
 38   803  1105   842   987   809   849   805   829    80  0.00
 39   802  1100   843   985   809   848   805   929    75  0.84
 40   803  1106   843   986   809   847   805   830    80  0.00
 41   863  1102   841   986   809   850   805   830   100  0.71
 42   802  1100   840   986   810   850   805   830    96  0.00
 43   802  1100   840   986   810   850   805   830    87  0.70
 44   803  1110   833   980   800   833   795   922     0  0.00
 45   805  1109   846   999   826   869   821   949   118  0.81
 46   808  1113   849   999   826   868   821   948   110  0.00
 47   809  1117   850   999   826   867   821   846   110  0.81
 48   802  1107   832   994   811   858   806   841   102  0.00
 49   793  1126   791   786   800   812   793   921   200  0.92
 50   860  1120   848   980   803   815   818   937   130  0.00
 51   798  1118   847   983   817   848   833   950    95  0.91
 52   803  1128   834   972   814   850   830   855   100  0.00
 53   803  1127   834   972   810   874   827   950   100  0.81
 54   803  1123   834   971   808   842   824   848    95  0.00
```

DATA SET 3

COMPUTER RUN A-3

```
  JOB DEF= ******                                                                                              PAGE    1
 PROC DEF=  NIXON
 DATA DEF=   DAVE                                                                                             BASIS  9.0
 ANALYSIS=  MULTR                                                                                                1/26/75
 DATA SET=     1         READ N=      54,       PROC N =      54,       REJ. N =       0,       SUM WT =      54


                      M U L T I P L E   L I N E A R   R E G R E S S I O N   A N A L Y S I S

GROUP NO  1
NO OF INDEPENDENT VARIABLES  9

EPS=  5.00000-11 FOR SINGULAR MATRIX TEST

DEPENDENT VARIABLE =      PPMSO2

MEANS AND STANDARD DEVIATIONS

     VARIABLE           MEAN  ST.DEVIATION

         AMI1       801.6154        6.4317
         AMO1      1115.1538       12.9203
         AMI2       841.4615       11.7549
         AMO2       977.6154       39.2113
         AMI3       809.8077        7.0144
         AMO3       844.7692       14.6923
         AMI4       813.6923       16.4530
         AMO4       835.3846       11.8695
        PSO2E         0.8131        0.0847
       PPMSO2       104.5769       30.4633

NORMAL MATRIX-

                1              2              3              4              5              6

ROW  1
        1034.1538       798.5386      1100.6152      2557.1538       264.0769       753.6924
         450.9231      1037.9462        -4.7192
ROW  2
           0.0000      4173.3948       320.1538     -2435.4614      -391.2307     -1031.0769
        1686.2307      -391.4617        -5.9623
ROW  3
           0.0000         0.0000      3454.4614     10503.6152       823.3076      1921.7693
        1624.6921      1585.3845        -6.9469
ROW  4
           0.0000         0.0000         0.0000     38438.1538      2907.0769      8201.6924
        4289.9231      4061.9462       -23.9592
ROW  5
           0.0000         0.0000         0.0000         0.0000      1230.0386      2130.8462
        1425.4614      1171.9231        -0.1946
ROW  6
           0.0000         0.0000         0.0000         0.0000         0.0000      5396.6155
        2924.1538      2829.3076        -4.5215
ROW  7
           0.0000         0.0000         0.0000         0.0000         0.0000         0.0000
        6767.5383      3649.0769        -9.0454
ROW  8
```

COMPUTER RUN A-16

```
       0.0000     0.0000     0.0000     0.0000     0.0000     0.0000
       0.0000  3522.1538    -7.9008
  ROW  9
       0.0000     0.0000     0.0000     0.0000     0.0000     0.0000
       0.0000     0.0000     0.1794

  CORRELATION MATRIX-

            1          2          3          4          5          6

  ROW  1
       1.0000     0.3844     0.5823     0.4056     0.2341     0.3190
       0.1704     0.5438    -0.3465     0.3391
  ROW  2
       0.3844     1.0000     0.0843    -0.1923    -0.1727    -0.2173
       0.3173     0.3890    -0.2179     0.5706
  ROW  3
       0.5823     0.0843     1.0000     0.9115     0.3994     0.4451
       0.3360     0.4545    -0.2791    -0.3572
  ROW  4
       0.4056    -0.1923     0.9115     1.0000     0.4228     0.5695
       0.2660     0.3491    -0.2886    -0.5468
  ROW  5
       0.2341    -0.1727     0.3994     0.4228     1.0000     0.8271
       0.4941     0.5630    -0.0131    -0.2531
  ROW  6
       0.3190    -0.2173     0.4451     0.5695     0.8271     1.0000
       0.4673     0.6490    -0.1453    -0.3272
  ROW  7
       0.1704     0.3173     0.3360     0.2660     0.4941     0.4673
       1.0000     0.7474    -0.2596     0.0024
  ROW  8
       0.5438     0.3890     0.4545     0.3491     0.5630     0.6490
       0.7474     1.0000    -0.3143     0.2421
  ROW  9
      -0.3465    -0.2179    -0.2791    -0.2856    -0.0131    -0.1453
      -0.2596    -0.3143     1.0000    -0.1630
  ROW 10
       0.3391     0.5706    -0.3572    -0.5468    -0.2531    -0.3272
       0.0024     0.2421    -0.1630     1.0000
```

COMPUTER RUN A-17

```
 JOB DEF= ******                                                                                       PAGE    2
 PROC DEF=  NIXON
 DATA DEF=   DAVE                                                                                      BASIS  4.0
 ANALYSIS=  MULTR                                                                                       1/26/75
 DATA SET=      1        READ N=     54,     PROC N =     54,     REJ. N =     0,     SUM WT =     54



 REGRESSION COEFFICIENTS-

     VARIABLE    COEFFICIENT    BETA COEFFICIENT

     CONSTANT     -1164.5826
         BMI1         2.4705              0.5216
         BMO1         0.1996              0.0847
         BMI2        -2.1128             -0.8153
         BMO2         0.0856              0.1101
         BMI3         1.0371              0.2388
         BMO3        -1.6164             -0.7796
         BMI4        -0.3973             -0.2146
         BMO4         1.9569              0.7625
        PSO2E       -30.8526             -0.0858

 STANDARD ERROR OF ESTIMATE.............. =        14.5036
 COEFFICIENT OF DETERMINATION............ =         0.8489
 COEFFICIENT OF DETERMINATION (ADJ)...... =         0.7639
 MULTIPLE CORRELATION COEFFICIENT........ =         0.9213
 MULTIPLE CORRELATION COEFFICIENT (ADJ) = =         0.8740


 STANDARD DEVIATIONS AND T VALUES OF
 REGRESSION COEFFICIENTS-

      VARIABLE    STD DEVIATION       T      STD DEV BETA       F
          BMI1           0.8028    3.08            0.1695    9.47
          BMO1           0.3836    0.52            0.1627    0.27
          BMI2           1.1025   -1.92            0.4254    3.67
          BMO2           0.3374    0.25            0.4342    0.06
          BMI3           0.9004    1.15            0.2073    1.33
          BMO3           0.5920   -2.73            0.2855    7.46
          BMI4           0.3267   -1.22            0.1765    1.48
          BMO4           0.6192    3.16            0.2412    9.99
         PSO2E          41.6647   -0.74            0.1158    0.55

 HIGH ORDER PARTIAL CORRELATION COEFF AND R2-DELETE

     VARIABLE    PARTIAL CORR COEF    R2-DELETE

         BMI1               0.6098       0.7594
         BMO1               0.1290       0.8463
         BMI2              -0.4320       0.8142
         BMO2               0.0633       0.8483
         BMI3               0.2767       0.8363
         BMO3              -0.5638       0.7784
         BMI4              -0.2908       0.8349
         BMO4               0.6200       0.7545
        PSO2E              -0.1820       0.8437
```

COMPUTER RUN A-18

```
ANALYSIS OF VARIANCE TABLE

    SOURCE   D.F.   SUM SQUARES  MEAN SQUARES      F

REGRESSION     9    19693.9971     2188.2219    9.99
     ERROR    16     3506.3491      219.1468
     TOTAL    25    23200.3462

CONFIDENCE LEVEL OF F(    9,   16) = 100.00%
```

COMPUTER RUN A-19

```
  JOB DEF= ******                                                                                          PAGE    3
 PROC DEF=  NIXON
 DATA DEF=   DAVE                                                                                         BASIS  4.0
 ANALYSIS=  MULTR                                                                                            1/26/75
 DATA SET=      1          READ N=      54,       PROC N =      54,       REJ. N =        0,       SUM WT =      54


 TABLE OF RESIDUALS

 OBS NO.          ACTUAL       PREDICTED        RESIDUAL

       1        120.0000        126.1367         -6.1367
       2        127.0000        127.9907         -0.9907
       3        130.0000        125.5020          4.4980
       4        140.0000        127.0292         12.9708
       5        141.0000        128.4920         12.5080
       6        127.0000        124.2415          2.7585
       7        100.0000         96.8331          3.1669
       8        132.0000        117.6582         14.3418
       9        110.0000        136.2034        -26.2034
      10         70.0000         89.8039        -19.8039
      11         80.0000         88.5561         -8.5561
      12         60.0000         53.0256          6.9744
      13         75.0000         84.8518         -9.8518
      14         65.0000         80.8247        -15.8247
      15         80.0000         91.1559        -11.1559
      16         90.0000         68.9140         21.0860
      17         92.0000         79.5277         12.4723
      18         95.0000         82.9416         12.0584
      19         75.0000         84.3802         -9.3802
      20        100.0000         94.2960          5.7040
      21         87.0000         94.8845         -7.8845
      22        118.0000        105.8397         12.1603
      23        110.0000        106.2301          3.7699
      24        200.0000        195.6723          4.3277
      25         95.0000        105.5764        -10.5764
      26        100.0000        102.4325         -2.4325

 DURBIN-WATSON D STATISTIC =      1.5653
```

COMPUTER RUN A-20

plant was considered in normal operating mode. The same model as in Section 1.1 was fitted to the 26 points having complete data. The results are given in A-16, 20. In this case the regression is significant at the one percent level and accounts for approximately 85 percent of the variability in SO_2 emission. In addition (See A-20), the model very nicely predicts SO_2 emission. Estimates of the coefficients in the model are given at the top of A-18. No attempt was made to reduce the set of independent variables to a smaller set and this may be possible through additional analyses. In view of the interdependence between the process parameters it is quite reasonable not to expect signs of particular coefficients to have some a'priori value (+ or -). In fact, the usual interpretation that a given regression coefficient measures the change in the dependent variable with the other variables held constant is not appropriate for highly correlated independent variables. The model simple presents the best linear fit over the range of values observed.

1.4 Data Sets (3) - (4)

These data, obtained from two similar plants of Texas Gulf, offered the opportunity to examine the effect of catalyst aging over time. Each set has one to three pieces of data for most months from March 1968 through December, 1973. In addition, these data contain values of SO_3, not previously considered in this section. Graphs of SO_3 and SO_2 versus time (B1, B2, B3) suggest, for the SO_2 data at least, that there are definite trends starting at what appears to be the catalyst cleaning month, CCM. In order to test the hypothesis that SO_2 is linearly related to time the following model was used:

$$Y = \alpha + \beta T$$

Where Y = mg SO_2/SCF and T = month since CCM. It was assumed that the CCM for Data Set (3) occurred in June, 1968, August, 1969, and August, 1972, and for Data Set (4) occurred July, 1968, August, 1969, and June, 1972. Two comparable samples were extracted from each of the data sets and all observations for a particular month were averaged to obtain one value for each T. The relationships are shown in B1, B2, B3, and the results are summarized in the following table:

SO_2 Versus T (from CCM)

	From (3)		From (4)	
	Sample 1	Sample 2	Sample 1	Sample 2
	13	14	12	17
	7.9	17.9	8.0	15.7
	121.1	36.3	127.8	33.1
correlation	.79	.87	.72	.78
std. error	24.7	47.4	29.0	72.4

Each of these regressions is significant at the five percent level. Interestingly, there is no significant difference between comparable samples from Data Sets (3) and (4) indicating that this measure of catalyst effect is the same for the two similar plants. The fact that the slopes for Sample 2 were about twice that for Sample 1 was apparently due to the fact that these plants burned "dirty sulfur" during the period October, 1972 through August, 1973. Unfortunately, this fact masks any conclusion of a catalyst effect difference over years. The SO_3 data for Sample 1 from (3) and (4) did not correlate with T; moreover, no trend was examined for Sample 2 from the two data sets due to any trend line being obscurred by "dirty sulfur" burning. A comparison of SO_3 means for the "dirty sulfur" period versus the other months for each of the data sets showed an extreme difference (for Data Set (2) these means were 22.7 and 1.4 respectively). A comparison of overall SO_2 and SO_3 means between Data Sets (2) and (3) showed no significant difference.

Analysis of variance of the SO_2 data (B4, B5, B6, B7) illustrates significant month and year effect for each of the data sets except for the month effect for Data Set (3). It has been suggested that a reason for this is the fact that there was a less controlled operation of Plant Number 1. The writer understands that the latter statement will be verified and the burning of "dirty sulfur" will be investigated on further contact

```
JOB DEF=  ******        STUDY OF CATALYST EFFECT SAMPLE 1                                                  PAGE    4
PROC DEF=   DAYC                                                                                            BASIS  4.0
DATA DEF=   NTX                                                                                            11/ 5/74
ANALYSIS=   TSA
DATA SET=     1         READ N=    107,     PROC N =    107,     REJ. N =      0,     SUM WT =    107
```

CONTACT ACID PLANT
SINGLE ABSORPTION (CHEMICO)

SO2

SO_2 EMISSIONS P.P.M.

COMPUTER RUN B-1

```
 ACTUAL   TREND   TREND          DATE  OBS.
 VALUE    VALUE   ERROR                 NO.
 X10
  259.0   162.8    96.2       3/28/68    1
  184.0   163.2    20.8       4/19/68    2
  163.0A  163.6    -0.6       4/26/68    3
  142.0   164.0   -22.0       5/ 1/68    4
  173.0   164.3     8.7       5/16/68    5
  125.0   164.7   -39.7       5/21/68    6
  227.0   165.1    61.9       5/31/68    7
  118.0   165.5   -47.5       7/22/68    8
  199.0   165.9    33.1       7/30/68    9
  214.0   166.2    47.8       8/ 6/68   10
  151.0   166.6   -15.6       8/15/68   11
  193.0   167.0    26.0       8/26/68   12
  137.0   167.4   -30.4       9/ 4/68   13
  103.0   167.8   -64.8       9/19/68   14
  117.0   168.2   -51.2       9/25/68   15
  138.0   168.5   -30.5      10/ 3/68   16
  134.0   168.9   -34.9      10/11/68   17
  151.0   169.3   -18.3      10/21/68   18
  157.0   169.7   -12.7      11/ 6/68   19
  181.0   170.1    10.9      11/15/68   20
  200.0   170.4    29.6      11/25/68   21
  138.0   170.8   -32.8      12/18/68   22
  186.0   171.2    14.8       1/ 6/69   23
  150.0   171.6   -21.6       1/27/69   24
  186.0   172.0    14.0       2/11/69   25
  192.0   172.3    19.7       2/24/69   26
  163.0   172.7    -9.7       3/ 3/69   27
  156.0   173.1   -17.1       3/13/69   28
  254.0   173.5    80.5       3/17/69   29
  159.0   173.9   -14.9       4/ 9/69   30
  225.0   174.3    50.7       4/30/69   31
  243.0   174.6    68.4       5/ 6/69   32
  229.0   175.0    54.0       5/28/69   33
  221.0   175.4    45.6       6/10/69   34
  254.0   175.8    78.2       7/ 1/69   35
  173.0   176.2    -3.2       9/11/69   36
  157.0   176.5   -19.5       9/17/69   37
  169.0   176.9    -7.9       9/26/69   38
  163.0   177.3   -14.3      10/13/69   39
  150.0   177.7   -27.7      10/16/69   40
  175.0   178.1    -3.1      10/20/69   41
  183.0   178.4     4.6      10/30/69   42
  153.0   178.8   -25.8      11/25/69   43
  314.0   179.2   134.8       1/15/70   44
  198.0   179.6    18.4       1/27/70   45
  119.0   180.0   -61.0       2/19/70   46
  349.0   180.4   168.6       3/24/70   47
  151.0   180.7   -29.7       4/28/70   48
  145.0   181.1   -36.1       5/12/70   49
   35.0   181.5  -146.5       8/ 4/70   50
  178.0   181.9    -3.9      10/20/70   51
  208.0   182.3    25.7      11/12/70   52
  183.0   182.6     0.4      11/18/70   53
  203.0   183.0    20.0      12/ 2/70   54
  192.0   183.4     8.6      12/11/70   55
  206.0   183.8    22.2      12/14/70   56
  110.0   184.2   -74.2       1/14/71   57
   83.0   184.5  -101.5       8/23/71   58
  111.0   184.9   -73.9       9/ 3/71   59
  215.0   185.3    29.7       9/10/71   60
  166.0   185.7   -19.7       9/24/71   61
  266.0   186.1    79.9      11/ 1/71   62
  315.0   186.5   128.5       1/ 3/72   63
  239.0   186.8    52.2       1/12/72   64
  220.0   187.2    32.8       2/21/72   65
  239.0   187.6    51.4       3/14/72   66
  195.0   188.0     7.0       3/20/72   67
  216.0   188.4    27.6       4/11/72   68
  190.0   188.7     1.3       4/25/72   69
  167.0   189.1   -22.1       5/ 1/72   70
  202.0   189.5    12.5       5/12/72   71
  194.0   189.9     4.1       5/16/72   72
  124.0   190.3   -66.3       6/16/72   73
  232.0   190.6    41.4       6/22/72   74
  202.0   191.0    11.0       6/28/72   75
   90.0   191.4  -101.4      10/ 2/72   76
    7.0   191.8  -184.8      10/11/72   77
   17.0   192.2  -175.2      10/12/72   78
  108.0   192.6   -84.6      10/13/72   79
  134.0   192.9   -58.9      10/20/72   80
   93.5A  193.3   -99.8      10/27/72   81
   53.0   193.7  -140.7      11/20/72   82
   16.0   194.1  -178.1      12/20/72   83
  201.0   194.5     6.5       2/ 6/73   84
  131.0   194.8   -63.8       2/20/73   85
  133.0   195.2   -62.2       3/ 1/73   86
  140.0   195.6   -55.6       3/ 8/73   87
  171.0   196.0   -25.0       3/14/73   88
  186.0   196.4   -10.4       4/ 2/73   89
  153.0   196.8   -43.8       4/17/73   90
  168.0   197.1   -29.1       5/ 2/73   91
  145.0   197.5   -52.5       5/17/73   92
  174.0   197.9   -23.9       6/ 7/73   93
  212.0   198.3    13.7       6/21/73   94
  183.0   198.7   -15.7       7/ 2/73   95
  344.0   199.0   145.0       7/25/73   96
  294.0   199.4    94.6       8/ 1/73   97
  265.0   199.8    65.2       8/22/73   98
  321.0   200.2   120.8       9/13/73   99
  306.0   200.6   105.4       9/24/73  100
  265.0   200.9    64.1       9/27/73  101
  311.0   201.3   109.7      10/10/73  102
  276.0   201.7    74.3      10/31/73  103
  317.0   202.1   114.9      11/14/73  104
  265.0   202.5    62.5      11/28/73  105
  203.0   202.9     0.1      12/ 4/73  106
  190.0   203.2   -13.2      12/20/73  107
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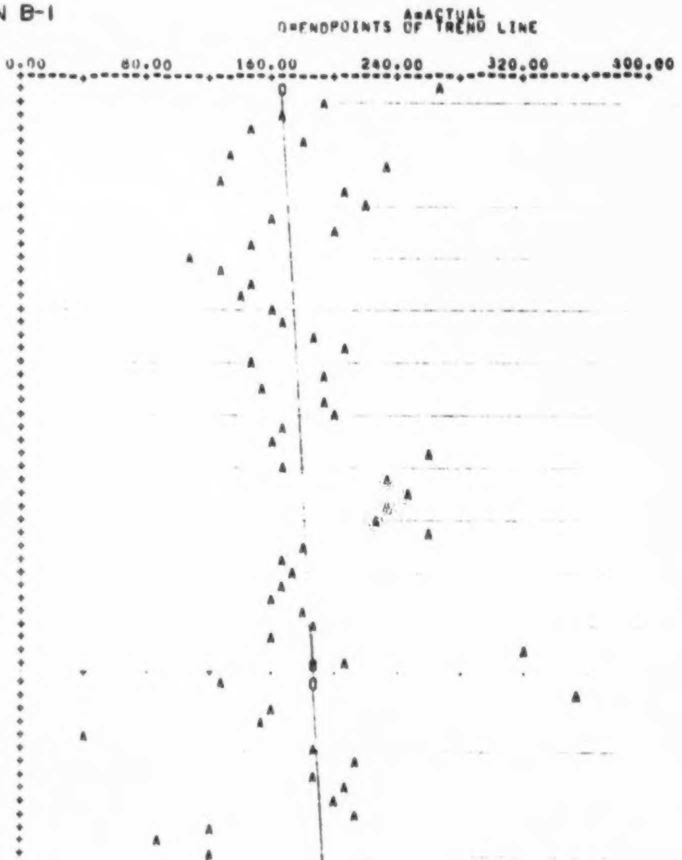

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```
   JOB DEF= ******        STUDY OF CATALYST EFFECT SAMPLE 2                                                        PAGE    4
  PROC DEF=   DAVE                                                                                                 BASIS  4.6
  DATA DEF=    NYC                                                                                                  11/ 5/74
  ANALYSIS=    TSA
  DATA SET=      1        READ N=    95,      PROC N =    95,      REJ. N =    0,     SUM WT =    95
```

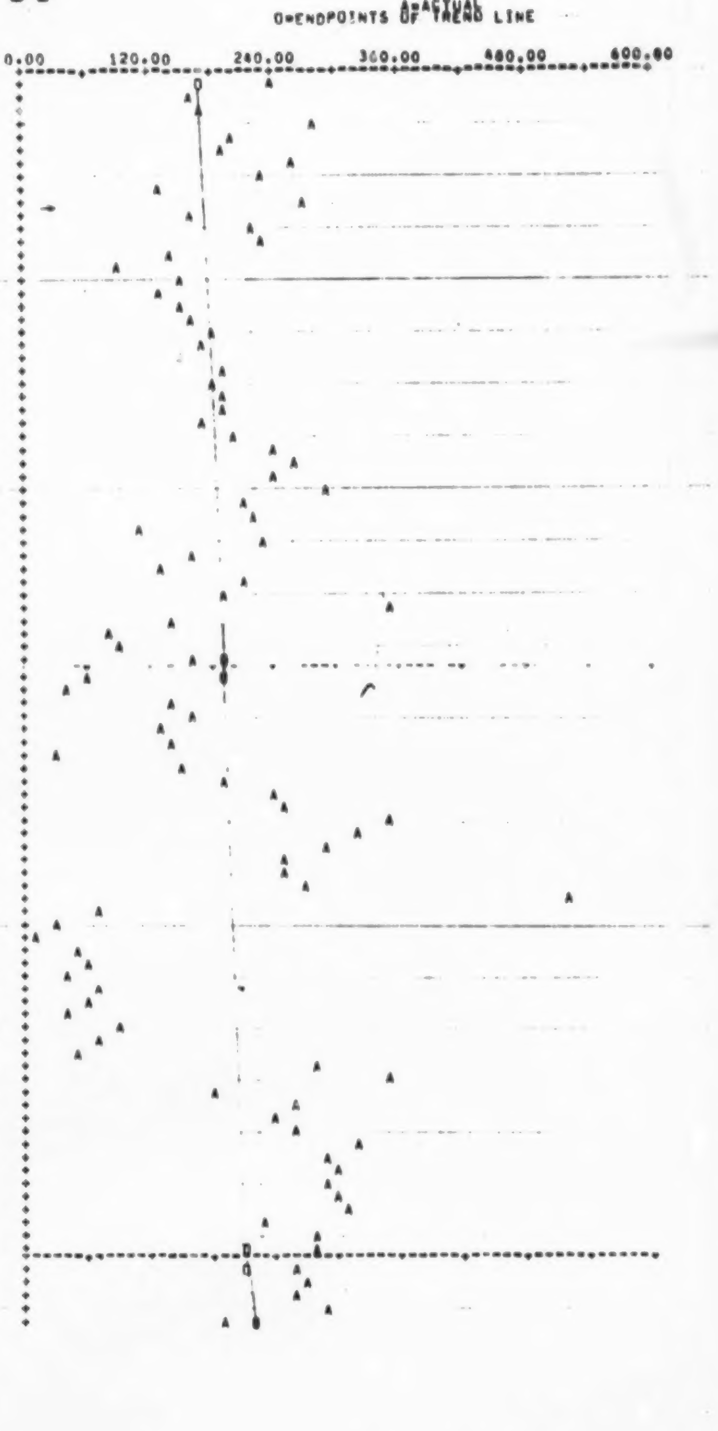
SO_2 EMISSIONS PPM.

SO2

COMPUTER RUN B-2

```
 ACTUAL    TREND    TREND                                  DATE    OBS.
 VALUE     VALUE    ERROR                                          NO.
  X10
 225.0     158.8     66.2                                 3/27/68    1
 151.0     159.3     -8.3                                 4/17/68    2
 159.0     159.8     -0.8                                 5/ 2/68    3
 267.0     160.3    106.7                                 5/14/68    4
 190.0     160.8     29.2                                 5/23/68    5
 179.0     161.3     17.7                                 5/30/68    6
 245.0     161.8     83.2                                 6/ 5/68    7
 217.0     162.3     54.7                                 6/13/68    8
 121.0     162.8    -41.8                                 6/19/68    9
 201.0     163.3     37.7                                 6/26/68   10
 151.0     163.8    -12.8                                 8/ 8/68   11
 206.0     164.3     41.7                                 8/16/68   12
 217.0     164.8     52.2                                 8/27/68   13
 131.0     165.3    -34.3                                 9/11/68   14
  79.0     165.8    -86.8                                 9/18/68   15
 144.0     166.3    -22.3                                 9/24/68   16
 120.0     166.8    -46.8                                10/ 9/68   17
 136.0     167.3    -31.3                                10/17/68   18
 149.0     167.8    -18.8                                10/22/68   19
 170.0     168.3      1.7                                11/14/68   20
 156.0     168.8    -12.8                                11/21/68   21
 144.0     169.3    -25.3                                12/19/68   22
 178.0     169.8      8.2                                 1/ 7/69   23
 170.0     170.3     -0.3                                 1/28/69   24
 177.0     170.8      6.2                                 2/25/69   25
 183.0     171.3     11.7                                 3/ 4/69   26
 156.0     171.8    -15.8                                 3/14/69   27
 191.0     172.3     18.7                                 4/10/69   28
 224.0     172.8     51.2                                 5/ 8/69   29
 247.0     173.3     73.7                                 5/27/69   30
 234.0     173.8     60.2                                 6/ 4/69   31
 282.0     174.3    107.7                                 6/19/69   32
 200.0     174.8     25.2                                 7/ 3/69   33
 205.0     175.3     29.7                                 7/22/69   34
  96.0     175.9    -79.9                                 9/10/69   35
 215.0     176.4     38.6                                 9/23/69   36
 150.0     176.9    -26.9                                10/ 9/69   37
 120.0     177.4    -57.4                                10/28/69   38
 195.0     177.9     17.1                                11/26/69   39
 175.0     178.4     -3.4                                 2/18/70   40
 337.0     178.9    158.1                                 3/31/70   41
 127.0     179.4    -52.4                                 4/ 3/70   42
  73.0     179.9   -106.9                                 6/ 7/70   43
  80.0     180.4   -100.4                                 6/17/70   44
 147.0     180.9    -33.9                                 8/20/70   45
  50.0     181.4   -131.4                                 8/21/70   46
  33.0     181.9   -148.9                                 8/25/70   47
 129.0     182.4    -53.4                                10/19/70   48
 153.0     182.9    -29.9                                11/10/70   49
 118.0     183.4    -65.4                                11/17/70   50
 130.0     183.9    -53.9                                11/25/70   51
  16.0     184.4   -168.4                                12/17/70   52
 138.0     184.9    -46.9                                 1/12/71   53
 178.0     185.4     -7.4                                 7/21/71   54
 227.0     185.9     41.1                                 8/25/71   55
 244.0     186.4     57.6                                10/20/71   56
 341.0     186.9    154.1                                12/ 6/71   57
 305.0     187.4    117.6                                 2/15/72   58
 280.0     187.9     92.1                                 3/15/72   59
 238.0     188.      49.6                                 3/21/72   60
 244.0     188.9     55.1                                 4/14/72   61
 258.0     189.4     68.6                                 4/25/72   62
 305.0     189.9    115.1                                 5/10/72   63
  64.0     190.4   -126.4                                 7/21/72   64
  18.0     190.9   -172.9                                 7/28/72   65
   3.0     191.4   -188.4                                 7/31/72   66
  39.0     191.9   -152.9                                 8/16/72   67
  53.0     192.4   -139.4                                 8/30/72   68
  30.0     192.9   -162.9                                 9/20/72   69
  61.0     193.4   -132.4                                10/ 5/72   70
  45.0     193.9   -148.9                                10/18/72   71
  33.0     194.4   -161.4                                11/ 1/72   72
  84.0     194.9   -110.9                                11/ 9/72   73
  60.0     195.4   -135.4                                11/20/72   74
  42.0     195.9   -153.9                                12/ 4/72   75
 265.0     196.4     68.6                                 2/ 5/73   76
 335.0     196.9    138.1                                 2/19/73   77
 173.0     197.4    -24.4                                 3/ 9/73   78
 248.0     197.9     50.1                                 3/14/73   79
 226.0     198.4     27.6                                 3/29/73   80
 247.0     198.9     48.1                                 4/11/73   81
 305.0     199.5    105.5                                 4/25/73   82
 284.0     200.0     84.0                                 5/10/73   83
 290.0     200.5     89.5                                 5/23/73   84
 284.0     201.0     83.0                                 5/31/73   85
 285.0     201.5     83.5                                 6/14/73   86
 302.0     202.0    100.0                                 7/12/73   87
 220.0     202.5     17.5                                 8/14/73   88
 270.0     203.0     67.0                                 8/20/73   89
 269.0     203.5     65.5                                 9/19/73   90

 248.0     204.0     44.0                                10/ 3/73   91
 255.0     204.5     50.5                                10/24/73   92
 252.0     205.0     47.0                                11/ 7/73   93
 284.0     205.5     78.5                                11/21/73   94
 181.0     206.0    -25.0                                12/13/73   95
```



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```
  JOB DEF= ******      STUDY OF CATALYST EFFECT SAMPLE 2                                                PAGE    1
 PROC DEF=   DAVE                                                                                       BASIS [illegible]
 DATA DEF=    VIX
 ANALYSIS=    TSA      READ N=    95,     PROC N =    95,     REJ. N =      0,     SUM WT =    95
 DATA SET=      1
```

ACID MIST SO3 Mg/S.C.F.

303

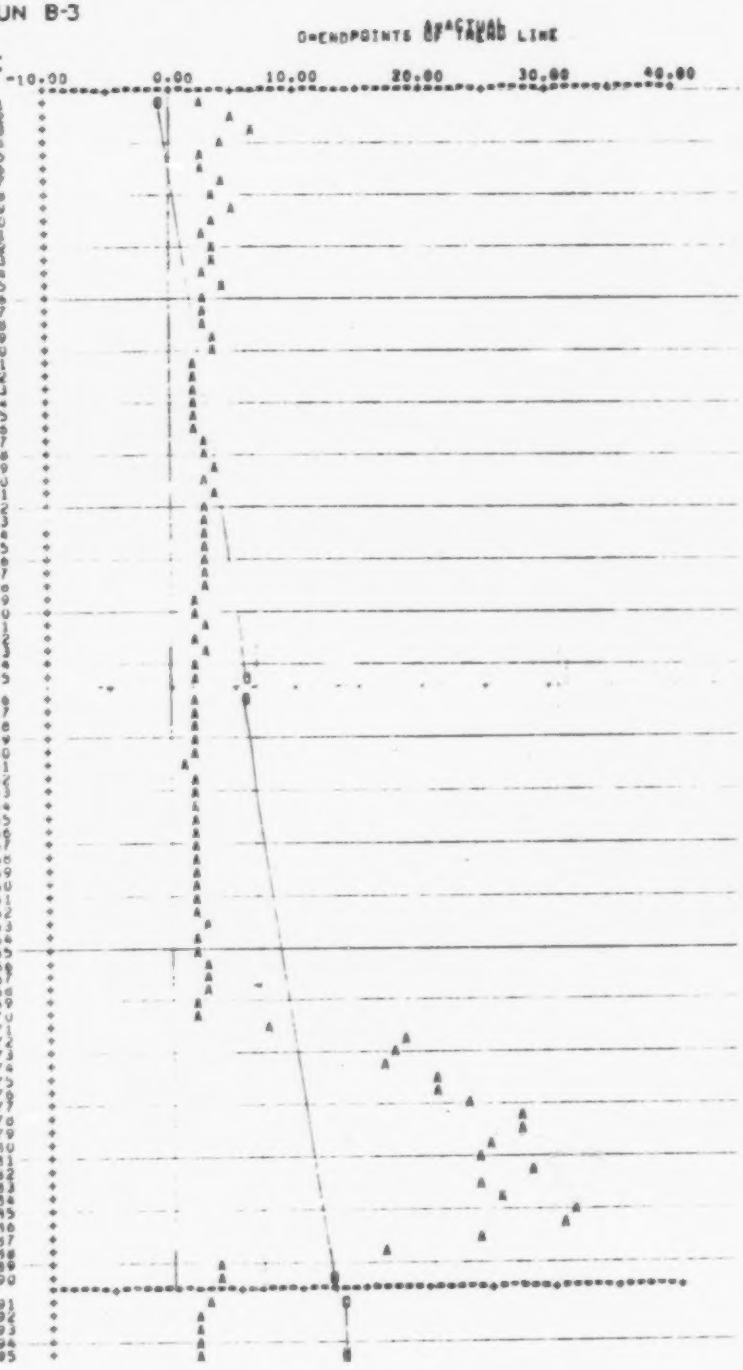
COMPUTER RUN B-3

```
 ACTUAL   TREND   TREND                        DATE    OBS.
  VALUE   VALUE   ERROR                                 NO.

    1.4    -1.8     3.2                     3/27/68      1
    4.3    -1.6     5.9                     4/17/68      2
    6.2    -1.5     7.8                     5/ 2/68      3
    3.0    -1.3     4.3                     5/14/68      4
    1.8    -1.2     3.0                     5/23/68      5
    1.7    -1.0     2.7                     5/30/68      6
    3.1    -0.9     4.0                     6/ 5/68      7
    2.4    -0.7     3.1                     6/13/68      8
    4.0    -0.6     4.6                     6/19/68      9
    2.7    -0.4     3.1                     6/26/68     10
    1.8    -0.3     2.1                     8/ 6/68     11
    2.8    -0.1     2.9                     8/16/68     12
    2.2 5.2E-02     2.2                     8/27/68     13
    1.8     0.2     1.6                     9/11/68     14
    3.1     0.4     2.7                     9/18/68     15
    1.8     0.5     1.3                     9/24/68     16
    1.6     0.7     0.9                    10/ 9/68     17
    1.7     0.8     0.8                    10/17/68     18
    2.5     1.0     1.5                    10/22/68     19
    2.2     1.1     1.1                    11/14/68     20
    1.0     1.3    -0.2                    11/21/68     21
    1.0     1.4    -0.5                    12/19/68     22
    1.1     1.6    -0.5                     1/ 7/69     23
    1.0     1.8    -0.8                     1/28/69     24
    1.2     1.9    -0.7                     2/25/69     25
    1.0     2.1    -1.0                     3/ 4/69     26
    1.3     2.2    -0.9                     3/14/69     27
    1.9     2.4    -0.5                     4/10/69     28
    2.2     2.5    -0.3                     5/ 8/69     29
    1.8     2.7    -0.9                     5/27/69     30
    2.3     2.8    -0.6                     6/ 4/69     31
    1.7     3.0    -1.3                     6/19/69     32
    1.8     3.1    -1.3                     7/ 3/69     33
    1.6     3.3    -1.7                     7/22/69     34
    1.9     3.4    -1.5                     9/16/69     35
    2.0     3.6    -1.6                     9/23/69     36
    1.5     3.8    -2.3                    10/ 9/69     37
    1.4     3.9    -2.5                    10/24/69     38
    0.9     4.1    -3.2                    11/26/69     39
    1.0     4.2    -3.2                     2/10/70     40
    1.5     4.4    -2.9                     3/31/70     41
    0.5     4.5    -4.0                     4/ 7/70     42
    1.5     4.7    -3.2                     6/ 7/70     43
    1.8     4.8    -3.0                     6/17/70     44
    0.9     5.0    -4.1                     8/20/70     45

    0.9A    5.1    -4.2                     8/21/70     46
    0.9     5.3    -4.4                     8/25/70     47
    0.6     5.5    -4.8                    10/19/70     48
    1.0     5.6    -4.6                    11/10/70     49
    0.6     5.8    -5.1                    11/17/70     50
    0.4     5.9    -5.5                    11/25/70     51
    0.8     6.1    -5.2                    12/17/70     52
    0.6     6.2    -5.6                     1/12/71     53
    0.9A    6.4    -5.5                     7/21/71     54
    1.1     6.5    -5.4                     8/25/71     55
    1.2     6.7    -5.5                    10/20/71     56
    0.5     6.8    -6.3                    12/ 6/71     57
    1.0     7.0    -6.0                     2/15/72     58
    1.0     7.2    -6.2                     3/15/72     59
    1.1     7.3    -6.2                     3/21/72     60
    0.6     7.5    -6.9                     4/14/72     61
    0.9     7.6    -6.7                     4/25/72     62
    1.4     7.8    -6.4                     5/16/72     63
    0.8     7.9    -7.1                     7/21/72     64
    0.7     8.1    -7.4                     7/28/72     65
    1.7     8.2    -6.6                     7/31/72     66
    1.4     8.4    -7.0                     8/16/72     67
    1.7     8.5    -6.9                     8/30/72     68
    0.8     8.7    -7.9                     9/20/72     69
    0.9     8.9    -8.0                    10/ 5/72     70
    6.7     9.0    -2.3                    10/18/72     71
   17.7     9.2     8.5                    11/ 1/72     72
   16.9A    9.3     7.5                    11/ 9/72     73
   16.0     9.5     6.5                    11/20/72     74
   19.9     9.6    10.2                    12/ 4/72     75
   20.3     9.8    10.5                     2/ 5/73     76
   22.8     9.9    12.9                     2/19/73     77
   26.5    10.1    16.4                     3/ 9/73     78
   27.1    10.2    16.8                     3/14/73     79
   24.0    10.4    13.6                     3/29/73     80
   23.7    10.5    13.2                     4/11/73     81
   27.6    10.7    16.9                     4/25/73     82
   23.6    10.9    12.7                     5/10/73     83
   25.4    11.0    14.4                     5/23/73     84
   30.0    11.2    18.8                     5/31/73     85
   29.9    11.3    18.5                     6/14/73     86
   23.0    11.5    11.5                     7/12/73     87
   15.6    11.6     4.0                     8/14/73     88
    2.7    11.8    -9.0                     8/28/73     89
    2.5    11.9    -9.4                     9/19/73     90

    2.0    12.1   -10.1                    10/ 3/73     91
    1.1    12.2   -11.2                    10/24/73     92
    0.7    12.4   -11.7                    11/ 7/73     93
    1.2    12.6   -11.4                    11/21/73     94
    1.1    12.7   -11.6                    12/13/73     95
```



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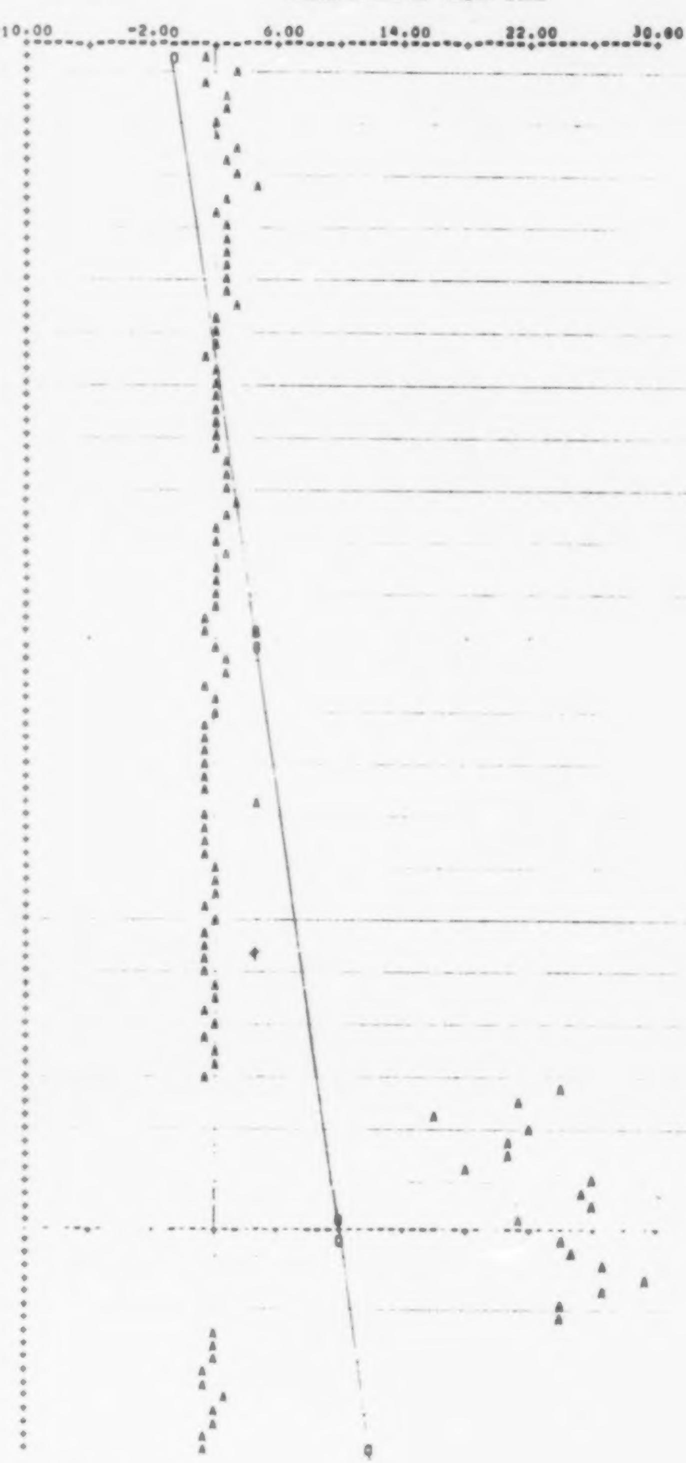
```
JOB DEF= ******     STUDY OF CATALYST EFFECT SAMPLE 1                                                PAGE    1
PROC DEF=   DAVE                                                                                     BASIS  4.0
DATA DEF=    NTX                                                                                     117 5/74
ANALYSIS=    TSA
DATA SET=      1    READ N=    107,    PROC N =    107,    REJ. N =     0,    SUM WT =    107
```

SO3

ACID MIST SO_3 Mg/SCF
COMPUTER RUN B-3A

ACTUAL VALUE	TREND VALUE	TREND ERROR	DATE	OBS. NO.
0.9	-1.6	2.5	3/20/68	1
2.6	-1.5	4.1	4/19/68	2
0.9	-1.3	2.2	4/29/68	3
2.3	-1.2	3.5	5/ 1/68	4
2.2	-1.1	3.3	5/10/68	5
1.3	-0.9	2.2	5/21/68	6
1.3	-0.8	2.1	5/31/68	7
2.7	-0.7	3.4	7/22/68	8
2.3	-0.6	2.9	7/30/68	9
3.0	-0.4	3.4	8/ 6/68	10
4.1	-0.3	4.4	8/15/68	11
2.2	-0.2	2.4	8/20/68	12
1.4	-0.1	1.5	9/ 4/68	13
2.1	5.== -0.2	2.1	9/19/68	14
1.6	0.2	1.4	9/25/68	15
2.2	0.3	1.9	10/ 3/68	16
1.7	0.4	1.3	10/11/68	17
2.0	0.5	1.5	10/21/68	18
2.2	0.7	1.5	11/ 6/68	19
2.4	0.8	1.6	11/15/68	20
1.1	0.9	0.2	11/25/68	21
1.2	1.0	0.2	12/10/68	22
1.3	1.2	0.1	1/ 8/69	23
0.8	1.3	-0.5	1/27/69	24
1.6	1.4	0.2	2/11/69	25
1.2	1.6	-0.4	2/24/69	26
1.3	1.7	-0.4	3/ 3/69	27
1.2	1.8	-0.6	3/13/69	28
1.0	1.9	-0.9	3/17/69	29
1.3	2.0	-0.7	4/ 9/69	30
1.6	2.2	-0.6	4/30/69	31
1.8	2.3	-0.5	5/ 6/69	32
2.1	2.4	-0.3	5/28/69	33
1.8	2.5	-0.7	6/10/69	34
2.6	2.7	-0.1	7/ 1/69	35
2.0	2.8	-0.8	9/11/69	36
1.0	2.9	-1.9	9/17/69	37
1.5	3.0	-1.5	9/26/69	38
1.7	3.1	-1.4	10/10/69	39
1.8	3.3	-1.5	10/18/69	40
1.6	3.4	-1.8	10/20/69	41
1.6	3.5	-1.9	10/30/69	42
1.2	3.6	-2.4	11/25/69	43
0.8	3.8	-3.0	1/13/70	44
0.8	3.9	-3.1	1/27/70	45
1.0	4.0	-3.0	2/19/70	46
1.9	4.1	-2.2	3/24/70	47
1.8	4.3	-2.5	4/28/70	48
0.8	4.4	-3.6	5/12/70	49
1.1	4.5	-3.4	8/ 4/70	50
1.2	4.6	-3.4	10/20/70	51
0.9	4.8	-3.9	11/12/70	52
1.0	4.9	-3.9	11/18/70	53
0.5	5.0	-4.5	12/ 2/70	54
0.7	5.1	-4.4	12/11/70	55
0.7	5.2	-4.5	12/14/70	56
0.7	5.4	-4.7	1/14/71	57
3.9	5.5	-1.6	4/23/71	58
0.6	5.6	-5.0	9/ 3/71	59
0.8	5.7	-4.9	9/16/71	60
0.8	5.9	-5.1	9/24/71	61
0.8	6.0	-5.2	11/ 1/71	62
1.4	6.1	-4.7	1/ 3/72	63
1.1	6.2	-5.1	1/12/72	64
1.1	6.4	-5.3	2/21/72	65
0.9	6.5	-5.6	3/14/72	66
1.0	6.6	-5.6	3/20/72	67
0.9	6.7	-5.8	4/11/72	68
0.8	6.9	-6.1	4/25/72	69
1.0	7.0	-6.0	5/ 1/72	70
0.7	7.1	-6.4	5/12/72	71
1.2	7.2	-6.0	5/18/72	72
1.6	7.4	-5.8	6/10/72	73
0.6	7.5	-6.9	6/22/72	74
1.1	7.6	-6.5	8/28/72	75
1.0	7.7	-6.7	10/ 2/72	76
1.7	7.8	-6.1	10/11/72	77
1.3A	8.0	-6.7	10/12/72	78
0.9	8.1	-7.2	10/13/72	79
23.1	8.2	14.9	10/20/72	80
20.8	8.3	12.5	10/27/72	81
15.4	8.5	6.9	11/20/72	82
21.5	8.6	12.9	12/26/72	83
19.8	8.7	11.1	2/ 6/73	84
20.2	8.8	11.4	2/20/73	85
17.6	9.0	8.6	3/ 1/73	86
25.1	9.1	16.0	3/ 8/73	87
25.0	9.2	15.8	3/14/73	88
25.1	9.3	15.8	4/ 2/73	89
20.7	9.5	11.2	4/17/73	90
23.2	9.6	13.6	5/ 2/73	91
24.1	9.7	14.4	5/17/73	92
24.1	9.8	14.3	6/ 7/73	93
24.4	10.0	14.4	6/21/73	94
26.0	10.1	15.9	7/ 2/73	95
23.4	10.2	13.2	7/25/73	96
23.5	10.3	13.2	8/ 1/73	97
1.6	10.4	-8.8	8/22/73	98
1.2	10.5	-9.3	9/13/73	99
1.1	10.7	-9.6	9/24/73	100
1.0	10.8	-9.8	9/27/73	101
0.8	10.9	-10.1	10/10/73	102
1.7	11.1	-9.4	10/31/73	103
1.1	11.2	-10.1	11/14/73	104
1.6	11.3	-9.7	11/20/73	105
0.9	11.4	-10.5	12/ 4/73	106
0.7	11.6	-10.9	12/20/73	107



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```
JOB DEF= ******            STUDY OF YEAR EFFECT SAMPLE 1                                                      PAGE     1
PROC DEF=   DAVE                                                                                              BASIS  4.0
DATA DEF=    NIX                                                                                               11/ 5/74
ANALYSIS= ANOVA1           READ N=    107,      PROC N =    107,      REJ. N =       0,      SUM WT =     107
DATA SET=      1


ONE-WAY ANALYSIS OF VARIANCE OF VAR=            SO2
 USING          *T1* AS THE SELECT (TREATMENT) VARIABLE.

 SUMMARY OF EACH OF THE  6 TREATMENT GROUPS.

 GROUP     VALUE OF
 NO.=J        *T1*     N(J)      MEAN(J)       SDEV(J)       VAR(J)

     1           1       21     168.0476       40.5937    1647.8476
     2           2       21     187.6667       35.4504    1256.7333
     3           3       13     190.8462       78.6711    6189.1410
     4           4        8     158.5000       70.8710    5022.7000
     5           5       20     158.0000       86.0918    7411.7895
     6           6       24     222.8750       68.3885    4676.9837

   I---------------------- ANALYSIS OF VARIANCE TABLE -----------------------I
   I                     SUMSQ      D. FREEDOM          MEAN SQ             F I
   I  BETWEEN                                                                 I
   I   GROUPS         62943.10            5.00         12588.62          3.07 I
   I  WITHIN                                                                  I
   I   GROUPS        405869.44           99.00          4099.69               I
   I                                                                          I
   I   TOTALS        468812.53          104.00                                I
   I--------------------------------------------------------------------------I

   CONFIDENCE LEVEL OF F(  5, 99)= 98.72%.
```

COMPUTER RUN B-4

```
JOB DEF= *******        STUDY OF YEAR EFFECT SAMPLE 2                                                                    PAGE    1
PROC DEF=   DAVE                                                                                                        BASIS  4.0
DATA DEF=    NIH                                                                                                         11/ 5/74
ANALYSIS= ANOVA1
DATA SET=      1        READ N=     95,     PROC N =     95,     REJ. N =       0,      SUM WT =     95


ONE-WAY ANALYSIS OF VARIANCE OF VAR=        502
USING        *TI* AS THE SELECT (TREATMENT) VARIABLE.

SUMMARY OF EACH OF THE  6 TREATMENT GROUPS.

GROUP      VALUE OF
NO.-J         *TI*     N(J)      MEAN(J)       SDEV(J)         VAR(J)

  1              1      22     173.6364       49.3207      2432.5201
  2              2      17     159.7059       45.5340      2073.3456
  3              3      13     120.6154       81.2685      6604.5897
  4              4       5     225.6000       76.8069      5899.3000
  5              5      18     131.2222      138.9374     19303.5948
  6              6      20     261.1500       39.7085      1576.7658

  I---------------------- ANALYSIS OF VARIANCE TABLE ----------------------I
  I BETWEEN            SUMSQ     D. FREEDOM         MEAN SQ              F  I
  I  GROUPS        232729.80           5.00        46545.96           7.60  I
  I  WITHIN                                                                 I
  I  GROUPS        545228.56          89.00         6126.16                 I
  I                                                                         I
  I  TOTALS        777958.36          94.00                                 I
  I-------------------------------------------------------------------------I

  CONFIDENCE LEVEL OF F(  5, 89)=100.00%.
```

COMPUTER RUN B-5

```
 JOB DEF= ******        STUDY OF MONTH EFFECT SAMPLE 1                                                         PAGE    1
PROC DEF=   DAVE                                                                                              BASIS 4.0
DATA DEF=    NIX                                                                                               117 5794
ANALYSIS= ANOVA1
DATA SET=      1        READ N=    107.      PROC N =    107.      REJ. N =       0.      SUM WT =    107


ONE-WAY ANALYSIS OF VARIANCE OF VAR=           SD2
 USING         *T1* AS THE SELECT (TREATMENT) VARIABLE.

 SUMMARY OF EACH OF THE 12 TREATMENT GROUPS.

 GROUP     VALUE OF
 NO.=J         *T1*     N(J)       MEAN(J)       SDEV(J)        VAR(J)

   1              1        7      216.0000       78.4241     6150.3333
   2              2        6      175.1667       40.5730     1646.1667
   3              3       10      205.9000       68.3381     4670.1000
   4              4        9      171.6667       42.3615     1794.5000
   5              5       12      180.0000       38.7768     1503.6364
   6              6        6      194.1667       39.6506     1572.1667
   7              7        5      219.6000       84.7720     7186.3000
   8              8        6      192.0000       92.2475     8509.6000
   9              9       12      186.6667       74.5146     5552.4242
  10             10       15      187.9333       79.5447     6327.3524
  11             11       10      197.8000       72.6159     5273.0667
  12             12        7      164.0000       69.3373     4807.6667


 I======================== ANALYSIS OF VARIANCE TABLE ========================I
 I                                                                            I
 I                    SUMSQ       D. FREEDOM           MEAN SQ             F  I
 I   BETWEEN                                                                  I
 I    GROUPS       45635.57            11.00           4148.69          0.91  I
 I                                                                            I
 I   WITHIN                                                                   I
 I   GROUPS       423176.97            93.00           4550.29                I
 I                                                                            I
 I   TOTALS       468812.53           104.00                                  I
 I                                                                            I
 I============================================================================I

 CONFIDENCE LEVEL OF F NOT COMPUTED. F≤1.0.
```

COMPUTER RUN B-6

```
  JOB DEF= ******        STUDY OF MONTH EFFECT SAMPLE 2                                                                PAGE    1
 PROC DEF=   DAVE                                                                                                   BASIS  4.0
 DATA DEF=    MIX                                                                                                    [illegible]
ANALYSIS= ANOVA1
DATA SET=       1        READ N=      95,      PROC N =      95,      REJ. N =       0,      SUM WT =      95


ONE-WAY ANALYSIS OF VARIANCE OF VAR=          SO2
 USING          *T1* AS THE SELECT (TREATMENT) VARIABLE.

 SUMMARY OF EACH OF THE 12 TREATMENT GROUPS.

 GROUP       VALUE OF
 NO.=J           *T1*      N(J)      MEAN(J)       SDEV(J)        VAR(J)

     1              1         3     162.0000       21.1660      448.0000
     2              2         5     251.4000       73.1785     5354.8000
     3              3         9     229.5556       56.2475     3163.7778
     4              4         7     217.5714       63.4872     4030.6190
     5              5        10     263.1000       97.1922     9446.3222
     6              6         9     199.7778       85.0805     7238.6944
     7              7         7     135.5714      111.7495    12487.9524
     8              8        11     148.8182       88.5436     7839.9636
     9              9         7     137.7143       81.7348     6680.5714
    10             10        11     150.6364       71.3054     5084.4545
    11             11        11     148.6364       76.4059     5837.8545
    12             12         5     144.8000      129.3859    16740.7000

       I********************** ANALYSIS OF VARIANCE TABLE *************************I
       I                                                                          I
       I                 SUMSQ     D. FREEDOM          MEAN SQ             F      I
       I BETWEEN                                                                  I
       I  GROUPS     193626.10          11.00         17602.37          2.50      I
       I                                                                          I
       I  WITHIN                                                                  I
       I  GROUPS     584332.26          83.00          7040.15                    I
       I                                                                          I
       I   TOTALS    777958.36          94.00                                     I
       I**************************************************************************I

  CONFIDENCE LEVEL OF F( 11, 83)= 99.09%.
```

332

COMPUTER RUN B-7

with Texas Gulf.

1.5 Data Set (5)

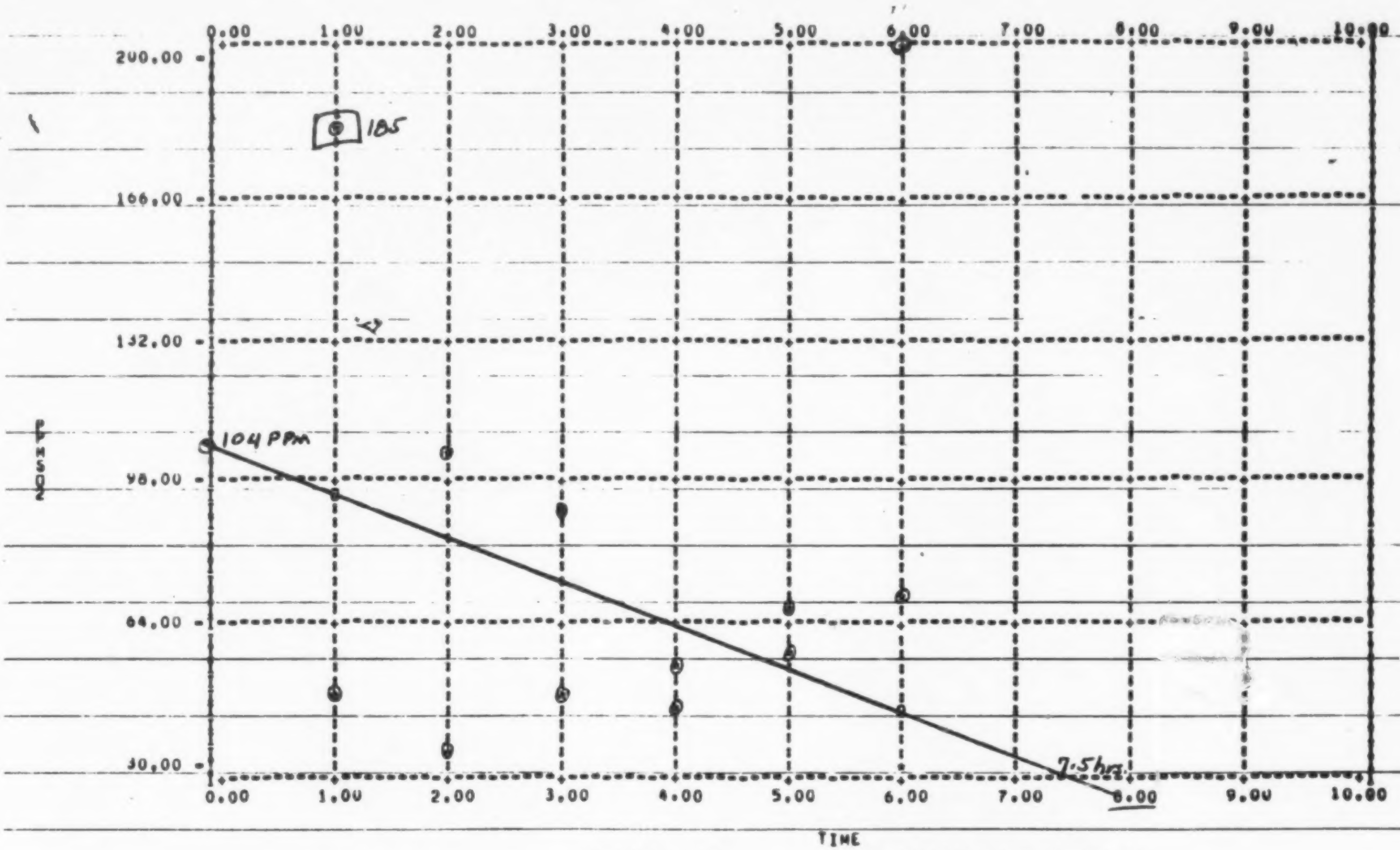
No attempt was made to find a model to fit the smooth curves shown in the referenced report (see (5) Section 1.1); however, a two-way analysis of variance was performed (B4 to B7) using tne six length of shutdown groups as one category and time into start-up as the other category. As a B4 to B7 shows there is a significant group and a significant time effect with SO_2 emission treated as the response variable. Regressions were obtained for each of the separate groups (C1 to C6) and the results are summarized below. The model $Y = \alpha + \beta T$ for each group.

Group			N	Correlation
1	- 10.3	106.8	12	-0.430
1-2	- 12.6	178.07	30	-0.154
2-6	- 92.4	757.0	18	-0.266
6-10	- 79.8	627.1	18	-0.372
10-15	-229.2	1417.3	24	-0.512*
15	-287.6	1969.0	36	-0.515*

*Significant at five percent level.

The use of these regression equations to predict the time after start-up at which the plant reaches the compliance limit is questionable. Since this time is the important variable, it was suggested that means and

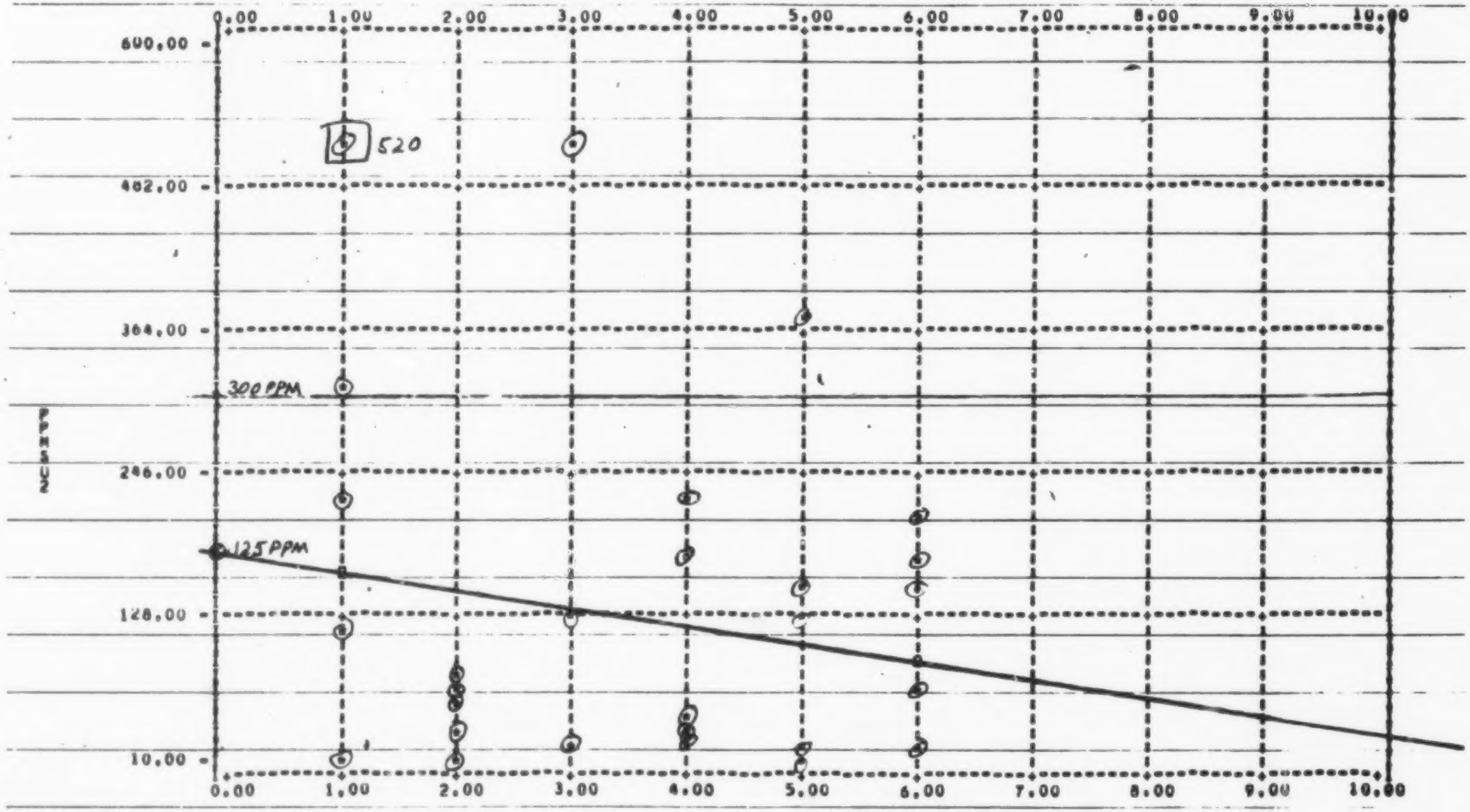
```
  JOB DEF= ******                                                                                PAGE    3
 PROC DEF=       K                                                                              BASIS  4.0
 DATA DEF=       F                                                                               11/19/74
ANALYSIS= REGRES
DATA SET=       1       READ N=     12,     PROC N =     12,     REJ. N =      0,     SUM WT =     12
```



```
SCATTER PLOT       O=REGRESSION LINE ENDPOINTS
```

COMPUTER RUN C-1

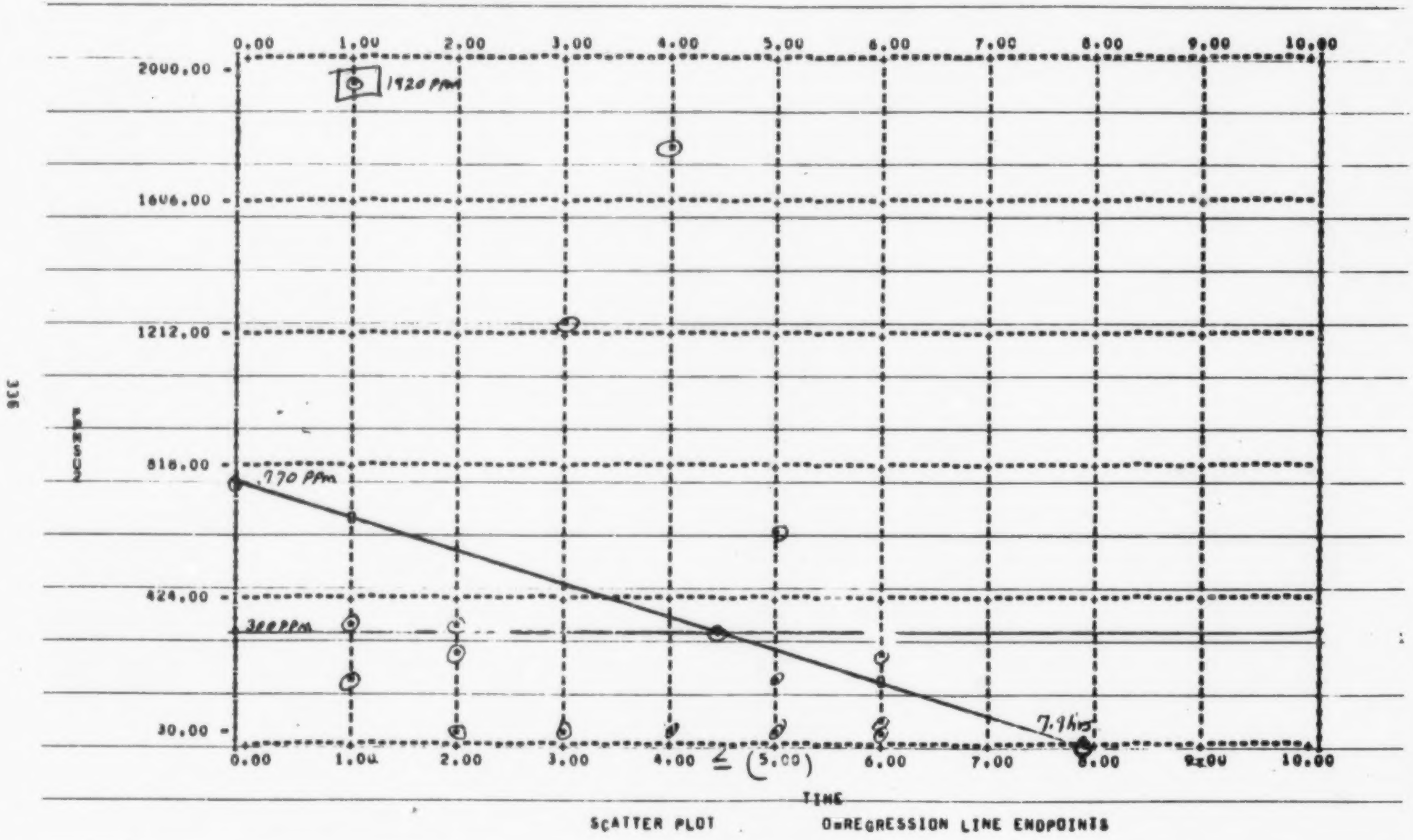
```
  JOB DEF= ******                                                                                          PAGE    4
 PROC DEF=      K                                                                                         BASIS  4.0
 DATA DEF=      F                                                                                          11/19/74
 ANALYSIS= REGRES
 DATA SET=      1       READ N=     30,     PROC N =     30,     REJ. N =      0,     SUM WT =     30
```



SCATTER PLOT   O=REGRESSION LINE ENDPOINTS

COMPUTER RUN C-2

```
  JOB DEF= ******
 PROC DEF=      K
 DATA DEF=      F
ANALYSIS= REGRES
 DATA SET=      1    READ N=    18,    PROC N =    18,    REJ. N =    0,    SUM WT =    18
```



SCATTER PLOT   O=REGRESSION LINE ENDPOINTS

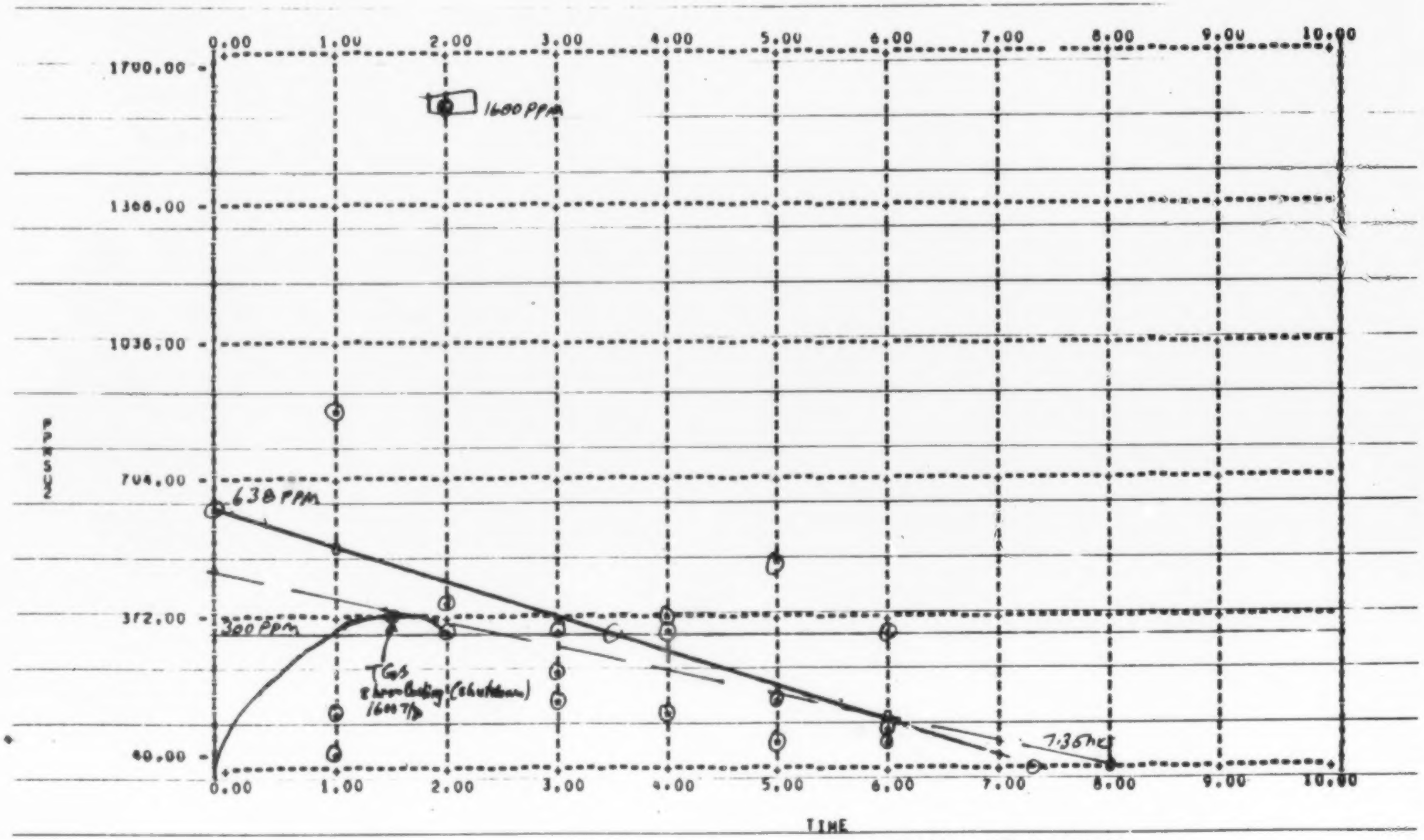
COMPUTER RUN C-3

JOB DEF= ******
PROC DEF= K
DATA DEF= P
ANALYSIS= REGRES
DATA SET= 1

READ N= 18, PROC N = 18, REJ. N = 0, SUM WT = 18

PAGE 3

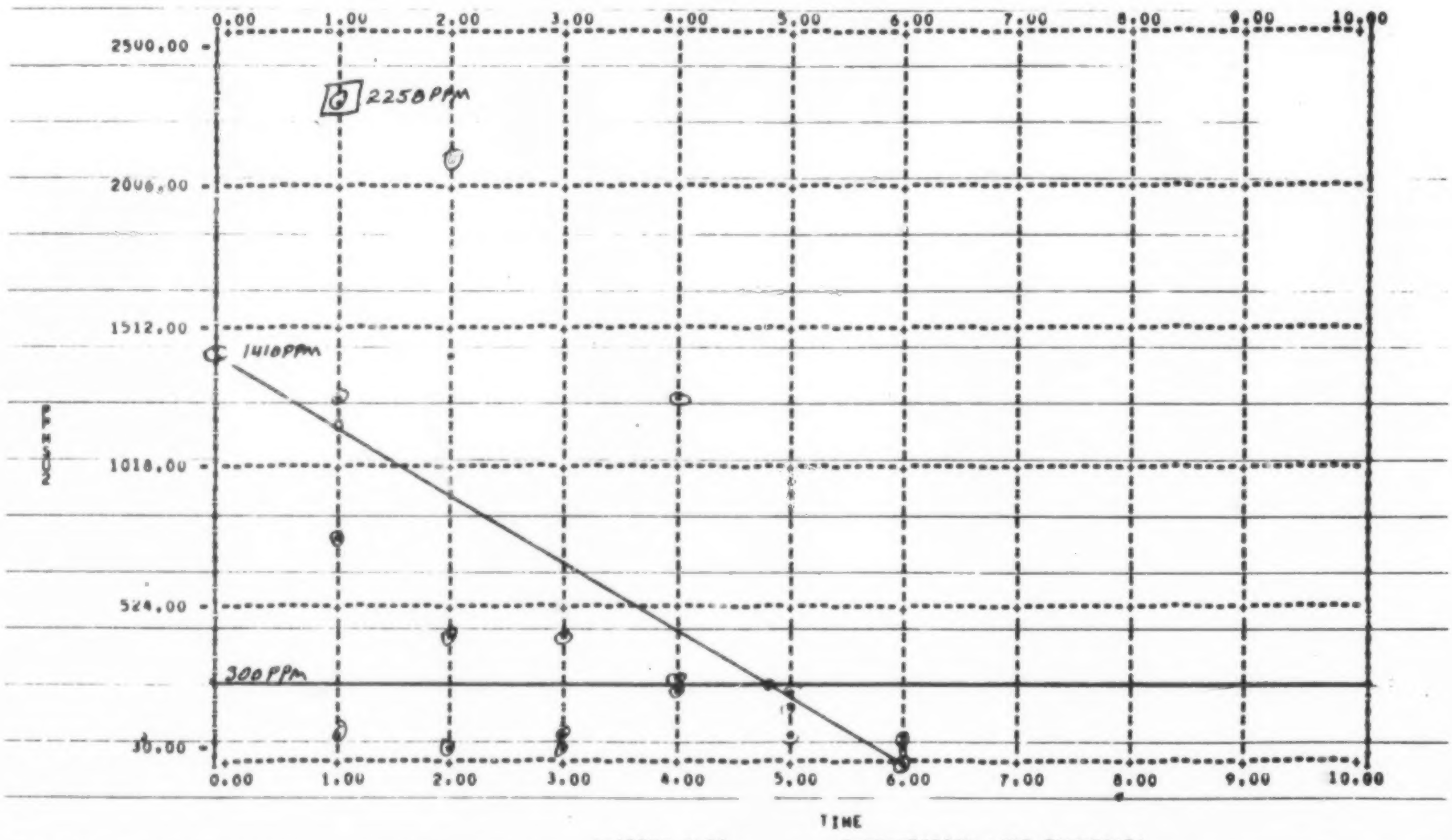
BASIS 4.0
11/19/74



SCATTER PLOT O=REGRESSION LINE ENDPOINTS

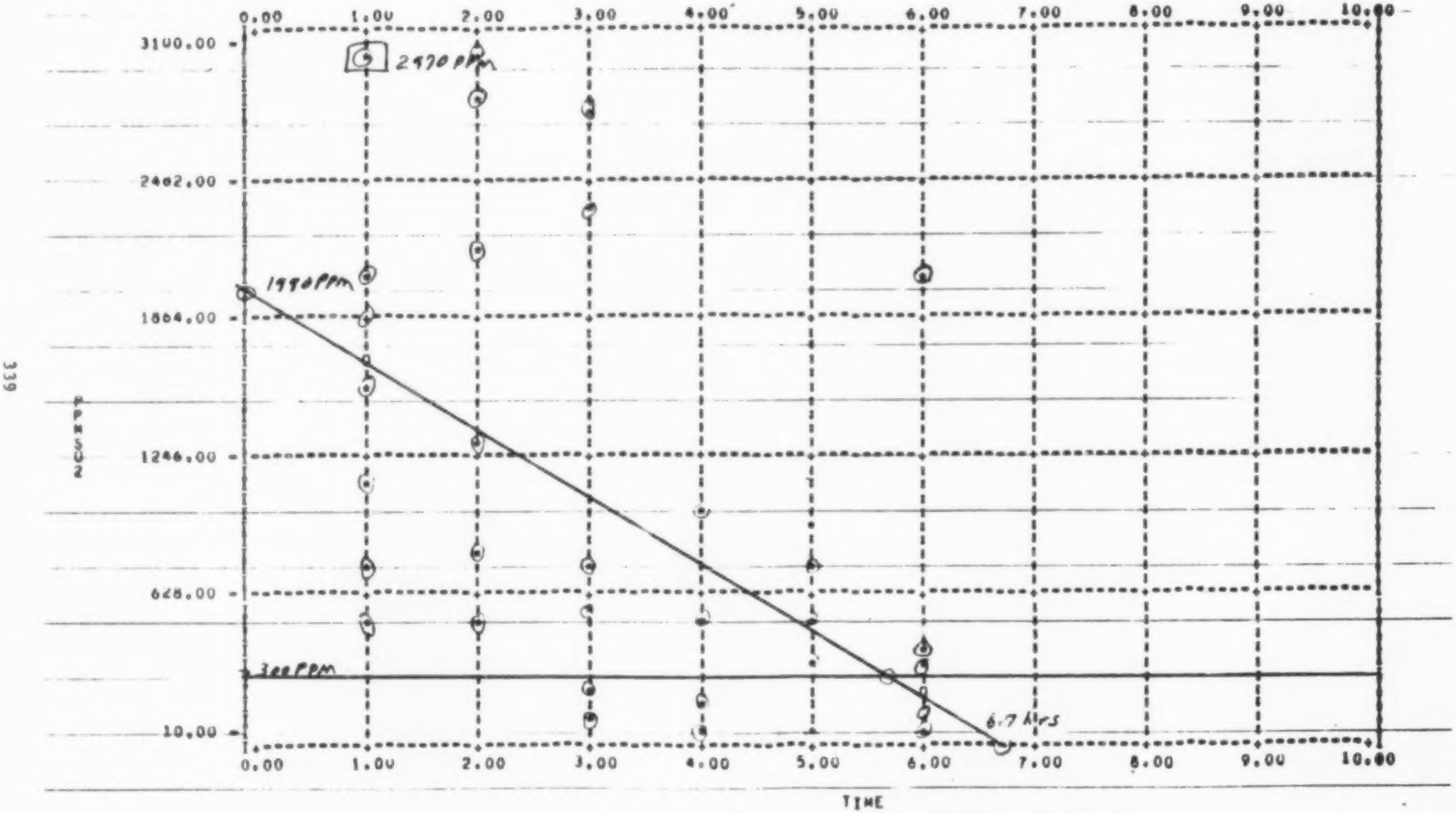
COMPUTER RUN C-4

```
  JOB DEF= ******                                                                                         PAGE    3
 PROC DEF=      K                                                                                        BASIS  4.0
 DATA DEF=      F                                                                                          11/19/74
ANALYSIS= REGRES
 DATA SET=      I          READ N=     24,        PROC N =     24,       REJ. N =      0,       SUM WT =     24
```



COMPUTER RUN C-5

```
 JOB DEF= ******                                                                                                    PAGE    4
PROC DEF=       K                                                                                                   BASIS  4.0
DATA DEF=       F                                                                                                    11/19/74
ANALYSIS= REGRES
DATA SET=       1      READ N=      36,      PROC N =      36,      REJ. N =      0,      SUM WT =      36
```



SCATTER PLOT   O=REGRESSION LINE ENDPOINTS

COMPUTER RUN C-6

variance of this quantity be computed

1.6 Problems and Recommendations

Major problems associated with this study were:

(a) The complicated nature of the process and relationships studied made full investigation of the acid plant system too time consuming for the type of task approved.

(b) The number of plants from which data was gathered was insufficient to discover plant to plant variability.

(c) All of the data looked at represented data gathered after the fact so that no experimentation in manipulating the process parameters was accomplished.

Any additional studies which may be performed on the SO_2 emissions should consider the need for expanded data collection mentioned above with the exception of (c) as it may be impossible to find plants willing to manipulate process parameters to force high emissions. At this writing it is felt that any future analysis of the SO_2 emissions as a function of process parameters should begin with data at approximately five minute intervals. The availability of this data would provide the ability to study a time-lag effect in explaining SO_2 emission. The high interdependence between the process parameters, and the observations of several continuous time charts on these parameters suggest a time-lag model might be appropriate.